



Applying point defect thermodynamics to Prussian Blue: Experiments and modelling

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ABSTRACT

Prussian Blue, $\text{Na}_{1+\xi}\text{Fe}[\text{Fe}(\text{CN})_6]$ is a promising low-cost cathode material for sodium-ion batteries (SIB). Despite its importance, the range of stoichiometry ξ of this mixed ionic and electronic conducting phase and the point defect structure are not known in adequate detail. An electrochemical cell using a sodium electrode, the solid Na^+ electrolyte NASICON and Prussian Blue is assembled. The course of the cell potential U_{cell} vs. ξ is measured by galvanostatic intermittent coulometric titration (GITT), the chemical diffusion coefficient $\bar{D}_{\text{Na}}$ of sodium is determined by evaluation of the cell potential transients.

Point defect thermodynamics is used to model relations between stoichiometry ξ , defect concentrations, cell potential U_{cell} , chemical potential and chemical diffusion coefficient $\bar{D}_{\text{Na}}$ of sodium. The thermal equilibrium between high-spin Fe^{3+} , low-spin Fe^{2+} , low-spin Fe^{3+} and high-spin Fe^{2+} , i.e. “electrons” and “holes”, is decisive for the electrochemical properties. U_{cell} vs. ξ and $\bar{D}_{\text{Na}}$ vs. ξ exhibit characteristic sigmoidal courses with an inflection point at $\xi = 0$. The equilibrium constant K_{cl} for electron-hole formation is obtained by fitting the experimental data. The corresponding Gibbs free enthalpy ΔG_{cl}^0 has a value of 0.3 eV, in accordance to Marcus-Hush theory, the energy of optically and thermally excited intervalence charge transfer. $\bar{D}_{\text{Na}}$ is in the order of 10^{-12} to 10^{-11} $\text{cm}^2 \text{ s}^{-1}$, the electronic charge carrier mobilities u_{e} and u_{h} in the order of 10^{-10} and 10^{-9} $\text{cm}^2 (\text{Vs})^{-1}$, indicating the presence of strongly localised small polarons. A full sodiation results in a Prussian White phase with a nominal composition $\text{Na}_2\text{Fe}[\text{Fe}(\text{CN})_6]$. A full desodiation seems to be impossible, ending up at a limiting composition of approximately $\text{Na}_{0.2}\text{Fe}[\text{Fe}(\text{CN})_6]$. The results of this study offer valuable insights for a better understanding the electrochemical (cycling) behaviour.

1. Introduction

The research activities on sodium-ion batteries (SIB) are highly increasing in the last decade. SIBs are discussed as a cost-effective and sustainable alternative to lithium-ion batteries (LIB), owing to the abundance and low cost of sodium. For a further increase of this economic advantage, low-cost cathode materials not based on nickel or cobalt oxides are also essential. Prussian Blue (PB) and Prussian Blue Analogues (PBA) are promising candidates. PB stands out for a high theoretical capacity of about $168.68 \text{ mAh g}^{-1}$ and low manufacturing costs.

PB features an open framework (Keggin) structure, built by $\text{Fe}^{2+}/\text{Fe}^{3+}$ cations and CN^- anions. In the case of PBA, the $\text{Fe}^{2+}/\text{Fe}^{3+}$

cations are substituted by other transition metal cations of comparable size, e.g. $\text{Mn}^{2+}/\text{Mn}^{3+}$, Cu^{2+} , $\text{Co}^{2+}/\text{Co}^{3+}$, Ni^{2+} . This structure enables an intercalation of the component sodium by a redox process in the transition metal sublattice and coupled Na^+ and electronic conduction.

However, despite the importance of this class of materials the available literature about the basic properties even of PB is very sparse. This includes the detailed stability ranges of the phases in the quasi-binary system $\text{Na}-\text{Fe}(\text{CN})_3$, as there are two phase transformations (Prussian white–Prussian Blue–Prussian Yellow). The actual Prussian Blue phase $\text{NaFe}[\text{Fe}(\text{CN})_6]$ is not at a margin of the phase field, but in the centre with a certain range non-stoichiometry regarding sodium. This does not allow to use a simple solid solution model to describe

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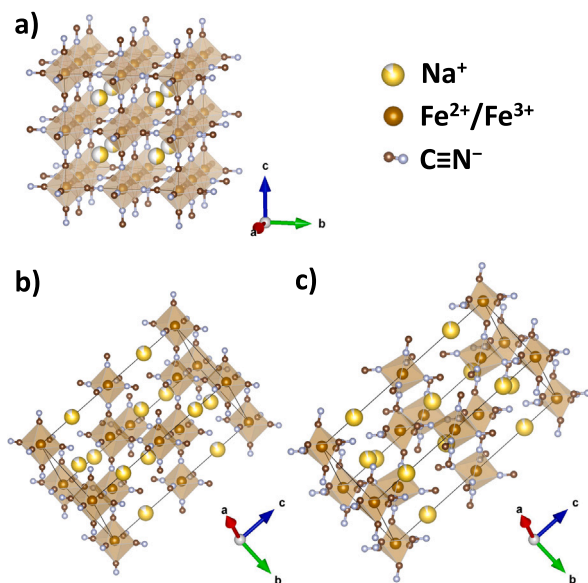


Fig. 1. (a) Lattice structure of the cubic Prussian Blue phase with a composition close to NaFe[Fe(CN)₆]. (b) Lattice structure of the trigonal Prussian White phase with a composition close to Na₂Fe[Fe(CN)₆] and straight connected Fe(CN)₆ octahedrons and (c) with alternating tilted Fe(CN)₆ octahedrons (visualisation by VESTA [6]).

the thermodynamic properties, as the point defect equilibria have to be considered. A detailed analysis of the point defect equilibria and their impact on the transport properties, as partial ionic and electronic conductivity and the chemical diffusion coefficient of sodium, is not sufficiently discussed in literature, yet.

A deeper insight into the point defect structure would help for future optimisation the properties of this class of materials, regarding extent of sodium intercalation and slow transport. This may help to overcome the limitations that hinder a full commercialisation. In this study we treat specifically the Prussian Blue phase by means of point defect thermodynamics to derive analytical expressions that join the composition of the material with the chemical potential of sodium, the battery cell potential and finally with transport properties as the chemical diffusion coefficient and partial conductivities. Marcus-Hush theory is considered to understand intervalence charge transfer processes.

2. Formal considerations

2.1. Structure of NaFe[Fe(CN)₆]

According to the literature, Prussian Blue crystallises in a cubic (Fm $\bar{3}$ m) structure [1–4]. The Fe²⁺ and Fe³⁺ ions are located on the 4a and 4b Wyckhoff positions. The CN⁻ ions are located on 24e positions, forming coordinative bridges between the Fe ions (Keggin structure) [5]. The Fe²⁺ ions are octahedrally coordinated by the C-side of the CN⁻ ion, the Fe³⁺ by the N-side, resulting in low-spin and a high-spin electronic configurations. The Na⁺ ions are located randomly on the 8c positions with 1/2 occupation, see Fig. 1(a).

This description corresponds to the ideal composition NaFe^{III}[Fe^{II}(CN)₆]. Firstly, there is a distinct broadness of the phase field regarding the sodium content, that can be described by a stoichiometry parameter ξ , i.e. Na_{1+ ξ} Fe[Fe(CN)₆]. The ideal composition of Prussian Blue is defined as unity, as it is advantageous for a description by point defect thermodynamics.

Secondly, depending on the preparation, there is a tendency to form Fe^{II}(CN)₆ vacancies in the structure. The free coordinative sites of the neighbouring Fe³⁺ ions are saturated by water molecules. Water can

also be intercalated on 8c (and 24e) sites can removed by drying in vacuum at elevated temperatures, water coordinated to Fe³⁺ ions cannot be removed below the decomposition temperature of Prussian Blue.

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2.2. Phase diagram of the system Na – Fe(CN)₃

The cage-like Keggin structure allows an intercalate and de-intercalate Na⁺ by a concurrent change of the ration between Fe²⁺ and Fe³⁺. Compounds are reported with compositions of Na₂Fe[Fe(CN)₆] to Fe(CN)₃. For simplicity, the stoichiometry parameter ξ , introduced originally for the Prussian Blue phase Na_{1+ ξ} Fe[Fe(CN)₆] is extended to a range of 1 to –1 to cover the whole system Na – Fe(CN)₃.

As mentioned before, an uptake of water as a third component is possible. At a higher water content also monoclinic phases are reported [8]. Thus, the following survey is restricted to sufficiently low water contents.

Compounds with a composition close to $\xi = 1$, i.e. Na₂Fe[Fe(CN)₆], referred as Prussian White, have a trigonal (R $\bar{3}$ h, rhomboedric) structure. It is related to the original cubic structure by a deformation of the unit cell along the [111] direction. In the literature two variants are found. The Fe(CN)₆ octahedrons can be connected in a straight or in a alternating tilted arrangement, see Fe–CN–Fe angles in Fig. 1(b) and (c) [7,9–12].

Compounds with a composition close to $\xi = -1$, i.e. Fe(CN)₃, are referred as Prussian Yellow or Prussian Brown. In the intermediate range at a composition of $\xi \approx -1/2$, the designation Prussian Green or Berlin Green is found. Depending on literature, this is referred to a two phase mixture of Prussian Blue and Prussian Yellow. Cubic structures (Fm $\bar{3}$ m) are also reported for these compounds, but the number of studies is rather sparse. [7,13–15], It is stated in some studies that the phase Fe(CN)₃ presumably does not exist, as CN⁻ ions are unstable against oxidation by Fe³⁺ [16].

The available structural data (for compounds with low water content) is compiled in Fig. 2 [2–4,7,9–15,17–22]. The unit cells of the trigonal phases are converted to a rhomboedric setup with the same number of formula units in the unit cell as in the cubic cell (see also supplemental material I):

$$a_{\text{rhom}} = \frac{1}{3} \sqrt{c_{\text{trig}}^2 + 12a_{\text{trig}}^2} \quad \text{and} \quad a_{\text{trig}} = b_{\text{trig}} \quad (1)$$

$$\cos \gamma_{\text{rhom}} = \frac{c_{\text{trig}}^2 - 6a_{\text{trig}}^2}{c_{\text{trig}}^2 + 12a_{\text{trig}}^2} \quad (2)$$

$$a_{\text{rhom}} = b_{\text{rhom}} = c_{\text{rhom}} \quad \text{and} \quad \alpha_{\text{rhom}} = \beta_{\text{rhom}} = \gamma_{\text{rhom}}$$

This allows to compare the extent of the structural changes due to the phase transitions.

Comparing the data for the cubic phases, the lattice constants are scattering for comparable compositions at least by $\pm 1\%$. Including the structural data from literature of compounds with slightly higher water contents, but still with a cubic structure, would considerably increase the total scatter.

Comparing the data for the trigonal (rhomboedric) phases, the rhomboedric lattice parameter of the two variants, featuring either straight connected Fe(CN)₆ octahedrons or alternating tilted octahedrons, differ significantly for a given composition. The phases with alternating tilted octahedrons have a 20% higher density ρ , respectively lower molar volume V_m (see also supplemental material II b and c).

The trigonal (rhomboedric) phase cannot be found for compositions $\xi < 0.7$. The change in lattice constant and angle for the transformation of the cubic phase to the trigonal phase with straight connected octahedrons is only very small, referring to the rhomboedric cell setup.

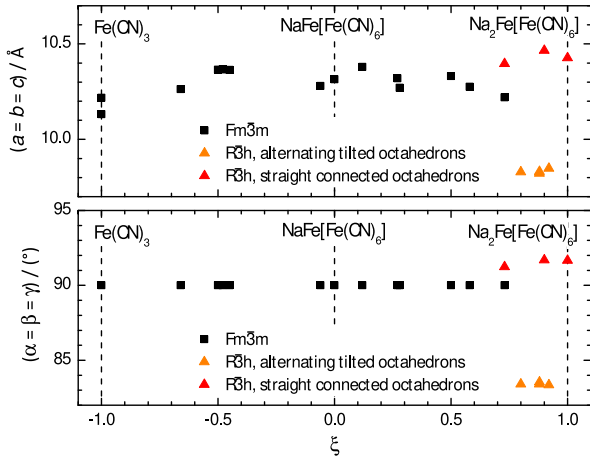


Fig. 2. Lattice constants and angles of Prussian Blue, Prussian White and Prussian Yellow phases with various composition compiled from literature and this study [2–4,7,9–15,17–22]. The unit cell of the trigonal phases is converted to a rhomboedric cell to be comparable to the cubic structures.

2.3. (Tentative) point defect model for Prussian Blue

In the following, we want to focus on the Prussian Blue phase $\text{Na}_{1+\xi}\text{Fe}[\text{Fe}(\text{CN})_6]$ with only small values of ξ . For the sake of simplification, the presence of $\text{Fe}^{\text{II}}(\text{CN})_6$ vacancies in the Keggin structure and water molecules occupying Na^+ sites are neglected. We will distinguish according to F. A. Kröger and H. J. Vinck between structural elements and building units, respectively, general ionic and electronic charge carriers, whose properties are accessible in electrochemical measurements [23,24].

Cationic point defects

Structural investigations by XRD result in a cubic face-centred structure with Na^+ on 8c sites and an occupation of 1/2. Interestingly, in theoretical studies using density functional theory (DFT) to calculate the crystallographic and electronic structure, it came out that the Na^+ ions should prefer 24e sites with an occupation of 1/6 in the square-like “gates”, formed by four CN^- , two Fe^{2+} and two Fe^{3+} ions [25,26]. Moderate temperatures (25 °C) result in a high Na^+ partial conductivity σ_{Na^+} in the order of 10^{-4} to $10^{-5} \text{ S cm}^{-1}$ (see supplemental material IV) [4]. This indicates a fast motion between the 8c sites (and 24e sites) and the presence of structural disorder [1,26]. Due to the structural disorder, regular and interstitial sites in the sodium sublattice, *i.e.* regular and irregular structural elements, cannot be distinguished. For the deviation of the chemical potentials, a Frenkel equilibrium can be formally expressed as follows:



Re-arranging Eq. (3) allows to identify the building units (point defects) $\{\text{Na}_{\text{i}}^{\cdot} - \text{V}_{\text{i}}^{\times}\}$ and $\{\text{V}_{\text{Na}}^{\cdot} - \text{Na}_{\text{Na}}^{\times}\}$, *i.e.* “sodium ions” $\text{Na}_{\text{i}}^{\cdot}$ and “vacant sites” $\text{V}_{\text{i}}^{\times}$:

$$0 \equiv \{\text{Na}_{\text{i}}^{\cdot} - \text{V}_{\text{i}}^{\times}\} + \{\text{V}_{\text{Na}}^{\cdot} - \text{Na}_{\text{Na}}^{\times}\} \quad (4)$$

Calculating the configurational entropy and considering incremental enthalpic and non-configurational entropic contributions per structural element, Eq. (3) yield the mass action law. According Kröger, the same result is obtained when assuming virtual chemical potentials, $\mu_{\text{i}} = \mu_{\text{i}}^0 + RT \ln x_{\text{i}}$, for the structural elements:

$$K_{\text{ion}} = \frac{x_{\text{Na}_{\text{i}}^{\cdot}}}{1 - x_{\text{Na}_{\text{i}}^{\cdot}}} \cdot \frac{x_{\text{V}_{\text{Na}}^{\cdot}}}{1 - x_{\text{V}_{\text{Na}}^{\cdot}}} \quad (5)$$

Hereby, K_{ion} denotes the equilibrium constant and x_{i} the molar fractions of the structural elements that are interdependent by the site balances and the condition of electroneutrality¹:

$$x_{\text{Na}_{\text{i}}^{\cdot}} + x_{\text{V}_{\text{i}}^{\times}} = 1 \quad \text{and} \quad x_{\text{V}_{\text{Na}}^{\cdot}} + x_{\text{Na}_{\text{Na}}^{\times}} = 1 \quad (6)$$

$$x_{\text{Na}_{\text{i}}^{\cdot}} - x_{\text{V}_{\text{Na}}^{\cdot}} = \xi \quad (7)$$

Considering Eqs. (4) and (5), the chemical potentials of the building units $\text{Na}_{\text{i}}^{\cdot}$ and $\text{V}_{\text{i}}^{\times}$ can be identified as²:

$$\mu_{\text{Na}_{\text{i}}^{\cdot}} \equiv \mu_{\text{Na}_{\text{i}}^{\cdot}} - \mu_{\text{V}_{\text{i}}^{\times}} = \mu_{\text{Na}_{\text{i}}^{\cdot}}^{\#} + RT \ln \frac{x_{\text{Na}_{\text{i}}^{\cdot}}}{1 - x_{\text{Na}_{\text{i}}^{\cdot}}} \quad (8)$$

$$\mu_{\text{V}_{\text{Na}}^{\cdot}} \equiv \mu_{\text{V}_{\text{Na}}^{\cdot}} - \mu_{\text{Na}_{\text{Na}}^{\times}} = \mu_{\text{V}_{\text{Na}}^{\cdot}}^{\#} + RT \ln \frac{x_{\text{V}_{\text{Na}}^{\cdot}}}{1 - x_{\text{V}_{\text{Na}}^{\cdot}}} \quad (9)$$

In the case of structural disorder, K_{ion} is unity. As expected, Eqs. (5), (6) and (7) result in identical molar fractions of interstitial and regular sites:

$$x_{\text{Na}_{\text{i}}^{\cdot}} = x_{\text{Na}_{\text{Na}}^{\times}} = \frac{1 + \xi}{2} \quad \text{and} \quad x_{\text{V}_{\text{Na}}^{\cdot}} = x_{\text{V}_{\text{i}}^{\times}} = \frac{1 - \xi}{2} \quad (10)$$

Inserting Eq. (10) in (8) and (9) yields the dependency of the chemical potentials of the building units on ξ :

$$\mu_{\text{Na}_{\text{i}}^{\cdot}} = \mu_{\text{Na}_{\text{i}}^{\cdot}}^{\#} + RT \ln \frac{1 + \xi}{1 - \xi} \quad (11)$$

$$\mu_{\text{V}_{\text{Na}}^{\cdot}} = \mu_{\text{V}_{\text{Na}}^{\cdot}}^{\#} - RT \ln \frac{1 + \xi}{1 - \xi} \quad (12)$$

For small deviations ξ from the stoichiometry, $x_{\text{Na}_{\text{i}}^{\cdot}}$ and $x_{\text{V}_{\text{Na}}^{\cdot}}$ does not change much (majority defects):

$$x_{\text{Na}_{\text{i}}^{\cdot}} = \frac{1}{x_{\text{V}_{\text{Na}}^{\cdot}}} = \frac{1 + \xi}{1 - \xi} \quad (13)$$

Electronic point defects

According to the available data in the literature, the electronic partial conductivity σ_{e^-} of nearly stoichiometric Prussian Blue is distinctly smaller compared to the Na^+ partial conductivity σ_{Na^+} . Values in the order of $10^{-7} \text{ S cm}^{-1}$ at 25 °C are reported (see supplemental material V) [4,27–32]. This is not surprising as the optical absorption and reflectivity of the material is not in line with typical small band gap semiconductors. There is a broad intervalence charge transfer band at about 708 nm (1.75 eV) due to an electron transition between an $\text{Fe}^{\text{II}}\text{-t}_{2\text{g}}$ and an $\text{Fe}^{\text{III}}\text{-t}_{2\text{g}}$ state. It is responsible for the blue colour of the material. This indicates the presence of rather localised electronic charge carriers, allowing only a hopping instead of a band conduction.

It makes the electronic partial conductivity σ_{e^-} a crucial parameter as it limits the chemical diffusion coefficient $\tilde{D}_{\text{Na}}$ of sodium and thus its intercalation/de-intercalation rate during charging and discharging when used as cathode material of a Na-ion-battery:

$$\tilde{D}_{\text{Na}} = \frac{1}{F^2} \frac{\sigma_{\text{Na}^+} \sigma_{\text{e}^-}}{\sigma_{\text{Na}^+} + \sigma_{\text{e}^-}} \frac{RT}{c_{\text{Na}}} \left(\frac{\partial \ln a_{\text{Na}}}{\partial \ln c_{\text{Na}}} \right)_T \quad (14)$$

Hereby, F denotes the Faraday constant, R the gas constant, T the temperature, c_{Na} the sodium concentration and $(\partial \ln a_{\text{Na}} / \partial \ln c_{\text{Na}})_T$ the thermodynamic factor.

A localisation of the electronic charge carriers implicates the presence of Fe ions with low-spin (LS) or high-spin configuration (HS) and an individual charge state of either +2 or +3. At a temperature T above 0 K, a thermal equilibrium has to be assumed:



¹ The molar fractions x_{i} and concentrations $c_{\text{i}} = x_{\text{i}}/V_{\text{m}}$ are connected by the molar volume V_{m} of Prussian Blue.

² A new standard potential at the stoichiometric composition (#) can be introduced, as it applies $x_{\text{Na}_{\text{i}}^{\cdot}}^{\#} = x_{\text{V}_{\text{Na}}^{\cdot}}^{\#}$ and $x_{\text{V}_{\text{Na}}^{\cdot}}^{\#} = x_{\text{Na}_{\text{Na}}^{\times}}^{\#}$:

$$\mu_{\text{Na}_{\text{i}}^{\cdot}}^{\#} = \mu_{\text{Na}_{\text{i}}^{\cdot}}^0 - \mu_{\text{V}_{\text{i}}^{\times}}^0 \quad \text{and} \quad \mu_{\text{V}_{\text{Na}}^{\cdot}}^{\#} = \mu_{\text{V}_{\text{Na}}^{\cdot}}^0 - \mu_{\text{Na}_{\text{Na}}^{\times}}^0$$

Considering the relative charge relative to the ideal ordered structure, one can write:

$$\text{Fe}_{\text{LS}}^{\times} + \text{Fe}_{\text{HS}}^{\times} \rightleftharpoons \text{Fe}_{\text{LS}}^{\cdot} + \text{Fe}_{\text{HS}}^{\cdot} \quad (16)$$

Thus, $\text{Fe}_{\text{LS}}^{\cdot}$ and $\text{Fe}_{\text{HS}}^{\cdot}$ are thermally generated irregular structural elements. Correspondingly, $\text{Fe}_{\text{LS}}^{\times}$ and $\text{Fe}_{\text{HS}}^{\times}$ are the regular structural elements. Re-arranging Eq. (16) allows to identify the building units (point defects) $\{\text{Fe}_{\text{HS}}^{\cdot} - \text{Fe}_{\text{HS}}^{\times}\}$ and $\{\text{Fe}_{\text{LS}}^{\cdot} - \text{Fe}_{\text{LS}}^{\times}\}$ that act as mobile charge carriers, i.e. “electrons” $e^{\cdot}$ and “holes” $h^{\cdot}$:

$$0 \rightleftharpoons \{\text{Fe}_{\text{HS}}^{\cdot} - \text{Fe}_{\text{HS}}^{\times}\} + \{\text{Fe}_{\text{LS}}^{\cdot} - \text{Fe}_{\text{LS}}^{\times}\} \quad (17)$$

Calculating the configurational entropy and considering incremental enthalpic and non-configurational entropic contributions per structural element, Eq. (16) yields a mass action law:

$$K_{\text{el}} = \frac{x_{\text{Fe}_{\text{HS}}^{\cdot}}}{1 - x_{\text{Fe}_{\text{HS}}^{\cdot}}} \cdot \frac{x_{\text{Fe}_{\text{LS}}^{\cdot}}}{1 - x_{\text{Fe}_{\text{LS}}^{\cdot}}} \quad (18)$$

This can also be obtained when assuming virtual chemical potentials, $\mu_i = \mu_i^0 + RT \ln x_i$, for the structural elements. The molar fractions of the structural elements are denoted by x_i and the equilibrium constant by K_{el} .¹ As well, the site balances and the condition of electroneutrality have to be taken into account:

$$x_{\text{Fe}_{\text{HS}}^{\cdot}} + x_{\text{Fe}_{\text{HS}}^{\times}} = 1 \quad \text{and} \quad x_{\text{Fe}_{\text{LS}}^{\cdot}} + x_{\text{Fe}_{\text{LS}}^{\times}} = 1 \quad (19)$$

$$x_{\text{Fe}_{\text{HS}}^{\cdot}} - x_{\text{Fe}_{\text{LS}}^{\cdot}} = \xi \quad (20)$$

Considering Eqs. (17) and (18), the chemical potentials of the building units $e^{\cdot}$ and $h^{\cdot}$ can be identified³:

$$\mu_{e^{\cdot}} \equiv \mu_{\text{Fe}_{\text{HS}}^{\cdot}} - \mu_{\text{Fe}_{\text{HS}}^{\times}} = \mu_{e^{\cdot}}^{\#} + RT \ln \frac{x_{\text{Fe}_{\text{HS}}^{\cdot}}}{1 - x_{\text{Fe}_{\text{HS}}^{\cdot}}} \quad (21)$$

$$\mu_{h^{\cdot}} \equiv \mu_{\text{Fe}_{\text{LS}}^{\cdot}} - \mu_{\text{Fe}_{\text{LS}}^{\times}} = \mu_{h^{\cdot}}^{\#} + RT \ln \frac{x_{\text{Fe}_{\text{LS}}^{\cdot}}}{1 - x_{\text{Fe}_{\text{LS}}^{\cdot}}} \quad (22)$$

The system of Eqs. (18), (19) and (20) can be solved and yield the molar fractions of the defect site structural elements:

$$x_{\text{Fe}_{\text{HS}}^{\cdot}} = -\frac{K_{\text{el}}}{1 - K_{\text{el}}} \left[1 - \frac{1}{\sqrt{K_{\text{el}}}} \exp \operatorname{arsinh} \left(\frac{(1 - K_{\text{el}})\xi}{2\sqrt{K_{\text{el}}}} \right) \right] \quad (23)$$

$$x_{\text{Fe}_{\text{LS}}^{\cdot}} = -\frac{K_{\text{el}}}{1 - K_{\text{el}}} \left[1 - \frac{1}{\sqrt{K_{\text{el}}}} \exp \operatorname{arsinh} \left(-\frac{(1 - K_{\text{el}})\xi}{2\sqrt{K_{\text{el}}}} \right) \right] \quad (24)$$

Inserting Eqs. (23) and (24) in Eqs. (21) and (22) yields the dependencies of the chemical potentials of the building units on ξ . Assuming only small values for the equilibrium constant K_{el} , Eqs. (23) and (24) can be significantly simplified⁴:

$$\mu_{e^{\cdot}} \approx \mu_{e^{\cdot}}^{\#} + RT \operatorname{arsinh} \frac{\xi}{2\sqrt{K_{\text{el}}}} \quad (25)$$

$$\mu_{h^{\cdot}} \approx \mu_{h^{\cdot}}^{\#} + RT \operatorname{arsinh} -\frac{\xi}{2\sqrt{K_{\text{el}}}} \quad (26)$$

For small deviations ξ from stoichiometry, there are large changes of $x_{e^{\cdot}}$ and $x_{h^{\cdot}}$ (minority defects):

$$x_{e^{\cdot}} = \frac{1}{x_{h^{\cdot}}} \approx \sqrt{K_{\text{el}}} \exp \operatorname{arsinh} \frac{\xi}{2\sqrt{K_{\text{el}}}} \quad (27)$$

The results are in accordance to the approach by C. Wagner [33]. This treatment assumes ideal behaviour, i.e. the activity coefficients of the building units are close to unity.

³ A new standard potential at the stoichiometric point (#) can be introduced, as it applies $x_{\text{Fe}_{\text{HS}}^{\cdot}}^{\#} = x_{\text{Fe}_{\text{HS}}^{\times}}^{\#}$ and $x_{\text{Fe}_{\text{LS}}^{\cdot}}^{\#} = x_{\text{Fe}_{\text{LS}}^{\times}}^{\#}$:

$\mu_{e^{\cdot}}^{\#} = \mu_{\text{Fe}_{\text{HS}}^{\cdot}}^0 - \mu_{\text{Fe}_{\text{HS}}^{\times}}^0$ and $\mu_{h^{\cdot}}^{\#} = \mu_{\text{Fe}_{\text{LS}}^{\cdot}}^0 - \mu_{\text{Fe}_{\text{LS}}^{\times}}^0$

⁴ For $K_{\text{el}} < 10^{-3}$ and $-0.2 < \xi < 0.2$ the error will not exceed 4%

Chemical potentials of Na^+ , $e^{\cdot}$ and Na

Performing electrochemical measurements, the building units (point defects) $\text{Na}^{\cdot}$ and $\text{V}^{\cdot}$, respectively, $e^{\cdot}$ and $h^{\cdot}$, cannot be distinguished principally. They appear as general ionic or electronic charge carriers, Na^+ and $e^{\cdot}$. Due to the thermal equilibria of the building units, the chemical potentials μ_{Na^+} and $\mu_{e^{\cdot}}$ of the general charge carriers depend on both, $\mu_{\text{Na}^{\cdot}}$ and $\mu_{\text{V}^{\cdot}}$, respectively, $\mu_{e^{\cdot}}$ and $\mu_{h^{\cdot}}$, see C. Wagner: [34]

$$\mu_{\text{Na}^+} \equiv \mu_{\text{Na}^{\cdot}} = -\mu_{\text{V}^{\cdot}} \quad (28)$$

$$\mu_{e^{\cdot}} \equiv \mu_{e^{\cdot}} = -\mu_{h^{\cdot}} \quad (29)$$

The chemical potential μ_{Na} of the neutral component Na consists of the chemical potentials of Na^+ and $e^{\cdot}$:

$$\mu_{\text{Na}} = \mu_{\text{Na}^+} + \mu_{e^{\cdot}} \quad (30)$$

Considering Eqs. (11), (12), (25), (26), (28) to (30) yields an expression for the chemical potential μ_{Na} of sodium as a function of ξ ⁵:

$$\mu_{\text{Na}} \approx \mu_{\text{Na}}^{\#} + RT \left(\ln \frac{1 + \xi}{1 - \xi} + \operatorname{arsinh} \frac{\xi}{2\sqrt{K_{\text{el}}}} \right) \quad (31)$$

2.4. Coulometric titration

A cell consisting of a Prussian Blue sample, connected to an inert metal, allowing only reversible exchange of electronic charge carriers $e^{\cdot}$ and to a metallic sodium electrode, separated by a pure Na^+ conductor with negligible electronic conductivity, allows the measurement of the chemical potential μ_{Na} of the component sodium in the sample vs. the chemical potential μ_{Na}^0 of metallic sodium, see Fig. 3:

$$\mu_{\text{Na}} - \mu_{\text{Na}}^0 = -FU_{\text{cell}} \quad (32)$$

By applying a current I_{titr} through the cell, it is possible to change the composition of the sample very precisely:

$$\Delta\xi = \frac{M}{m} \frac{1}{F} \int I_{\text{titr}} dt \quad (33)$$

The molar mass of a formula unit of Prussian Blue is denoted by M , the sample mass by m and the change in stoichiometry by $\Delta\xi$. The chemical potential of sodium and thus the cell potential is continuously changing as a function of the sodium content in a single phase field. When reaching a two phase region in the phase diagram, it keeps constant due to the thermodynamic conditions for a two phase equilibrium.

In the phase field of Prussian Blue, assuming only small deviations ξ from stoichiometry, the cell potential U_{cell} can be calculated by combining Eqs. (31) and (32):

$$-FU_{\text{cell}} = \mu_{\text{Na}}^{\#} - \mu_{\text{Na}}^0 + RT \operatorname{arsinh} \frac{\xi}{2\sqrt{K_{\text{el}}}} \quad (34)$$

For values of $K_{\text{el}} < 10^{-3}$ and small deviations ξ from stoichiometry, the term $\ln((1 + \xi)/(1 - \xi))$ in Eq. (31) can be safely neglected (~1% error). A characteristic S-shaped course is obtained, see Fig. 4(a). The slope $(\partial U_{\text{cell}}/\partial \xi)_T$ of the functional course U_{cell} vs. ξ yields as:

$$\left(\frac{\partial U_{\text{cell}}}{\partial \xi} \right)_T = -\frac{RT}{F} \frac{1}{\sqrt{4K_{\text{el}} + \xi^2}} \quad (35)$$

There is an inflection point at the stoichiometric composition ($\xi = 0$) due to the arsinh function. The slope at the inflection point depends on only the equilibrium constant of the electron-hole-equilibrium in Eq. (18):

$$\left(\frac{\partial U_{\text{cell}}}{\partial \xi} \right)_{T, \xi=0} = -\frac{RT}{F} \frac{1}{2\sqrt{K_{\text{el}}}} \quad (36)$$

⁵ $\mu_{\text{Na}}^{\#} = \mu_{\text{Na}^+}^{\#} + \mu_{e^{\cdot}}^{\#}$

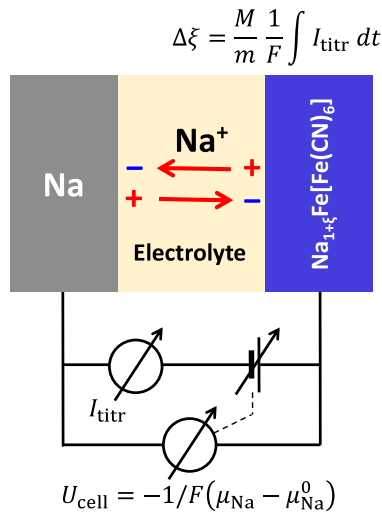


Fig. 3. Schematic setup for a coulometric titration. The electrolyte only allows Na^+ but no electronic conduction. There are no other parasitic redox reactions at the electrode interfaces.

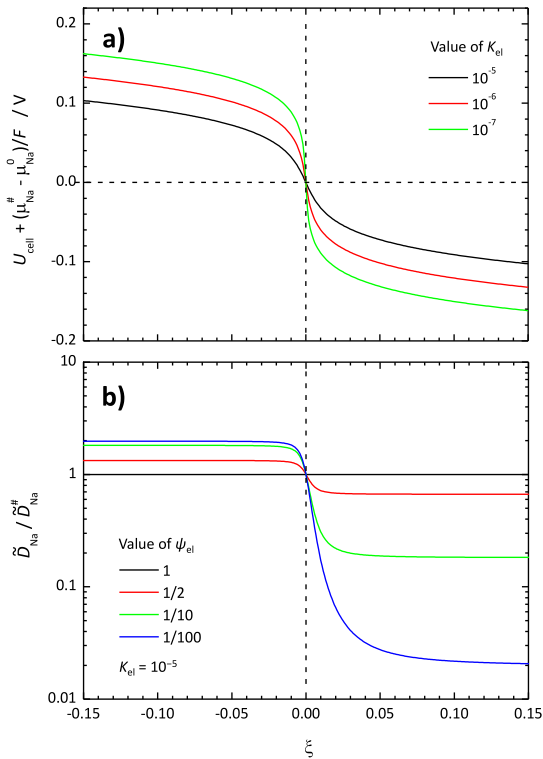


Fig. 4. (a) Course of the (relative) cell potential $U_{\text{cell}} + (\mu_{\text{Na}}^{\#} - \mu_{\text{Na}}^0)/F$ vs. ξ for various values of the equilibrium constant K_{el} . (b) Course of the (relative) chemical diffusion coefficient $\tilde{D}_{\text{Na}}^{\#} / \tilde{D}_{\text{Na}}^0$ vs. ξ for various values of the mobility ratio $\psi_{\text{el}} = u_{\text{e}'} / u_{\text{h}}$ and $K_{\text{el}} = 10^{-5}$. Data calculated according to the point defect model at $T = 298$ K.

The thermodynamic factor in Eq. (14) also depends on the slope $(\partial U_{\text{cell}} / \partial \xi)_T$:

$$\left(\frac{\partial \ln a_{\text{Na}}}{\partial \ln c_{\text{Na}}} \right)_T = - \frac{F(1 + \xi)}{RT} \left(\frac{\partial U_{\text{cell}}}{\partial \xi} \right)_T \quad (37)$$

Thus, it can be calculated according to the point defect model by considering Eq. (35) as:

$$\left(\frac{\partial \ln a_{\text{Na}}}{\partial \ln c_{\text{Na}}} \right)_T = \frac{1 + \xi}{\sqrt{4K_{\text{el}} + \xi^2}} \quad (38)$$

The thermodynamic factor should reach a maximum value at the stoichiometric composition ($\xi = 0$):

$$\left(\frac{\partial \ln a_{\text{Na}}}{\partial \ln c_{\text{Na}}} \right)_{T, \xi=0} = \frac{1}{2\sqrt{K_{\text{el}}}} \quad (39)$$

The Gibbs free reaction enthalpy ΔG_{el}^0 of the electron–hole–equilibrium can be calculated according:

$$\Delta G_{\text{el}}^0 = -RT \ln K_{\text{el}} \quad (40)$$

2.5. Chemical diffusion coefficient of Na

The chemical diffusion coefficient $\tilde{D}_{\text{Na}}$ of sodium depends on the thermodynamic factor $(\partial \ln a_{\text{Na}} / \partial \ln c_{\text{Na}})_T$ and the partial conductivities σ_{Na^+} and σ_{e^-} of the charge carriers Na^+ and e^- . The latter depend principally on the molar fractions of the building units acting as mobile charge carriers:

$$\sigma_{\text{Na}^+} = \frac{F}{V_m} (u_{\text{Na}} \cdot x_{\text{Na}^+} + u_{\text{V}'} \cdot x_{\text{V}'}) \quad (41)$$

$$\sigma_{\text{e}^-} = \frac{F}{V_m} (u_{\text{e}'} \cdot x_{\text{e}'} + u_{\text{h}} \cdot x_{\text{h}}) \quad (42)$$

The electrical mobility of the mobile charge carriers are denoted by u_{Na^+} , $u_{\text{V}'}$, $u_{\text{e}'}$ and u_{h} .

Due to the structural disorder, u_{Na^+} and $u_{\text{V}'}$ cannot be distinguished. For small deviations from stoichiometry, the molar fractions of the building units in Eq. (13) does not change much. Thus, the partial conductivity σ_{Na^+} is nearly constant:

$$\sigma_{\text{Na}^+} \approx \frac{F}{V_m} u_{\text{Na}^+} \quad (43)$$

The partial conductivity σ_{e^-} should depend significantly on ξ . Inserting Eq. (27) in (42) yields:

$$\sigma_{\text{e}^-} = \frac{F}{V_m} \sqrt{K_{\text{el}}} \left(u_{\text{e}'} \exp \operatorname{arsinh} \frac{\xi}{2\sqrt{K_{\text{el}}}} + u_{\text{h}} \exp \operatorname{arsinh} - \frac{\xi}{2\sqrt{K_{\text{el}}}} \right) \quad (44)$$

The chemical diffusion coefficient $\tilde{D}_{\text{Na}}$ can be derived by inserting Eqs. (43), (38) and (44) in (14). According to the available literature, the value of the partial conductivity σ_{Na^+} exceeds the value of σ_{e^-} by orders of magnitude. Thus, due to the Nernst–Planck coupling, the partial conductivity σ_{Na^+} actually cancels out⁶:

$$\tilde{D}_{\text{Na}} = \frac{RT}{2F} \left[u_{\text{e}'} + u_{\text{h}} + (u_{\text{e}'} - u_{\text{h}}) \tanh \operatorname{arsinh} \frac{\xi}{2\sqrt{K_{\text{el}}}} \right] \quad (45)$$

A S-shaped step-like course of $\tilde{D}_{\text{Na}}$ vs. ξ can be expected for non-identical mobilities $u_{\text{e}'}$ and u_{h} , due to the tanh function, see Fig. 4(b). The limiting values are $\tilde{D}_{\text{Na}}(\xi \ll 0) = u_{\text{h}} RT/F$ and $\tilde{D}_{\text{Na}}(\xi \gg 0) = u_{\text{e}'} RT/F$. An inflection point is situated at the stoichiometric composition ($\xi = 0$). If the mobilities are equal, the dependence on the stoichiometry is cancelled out.⁷

⁶ Considering the relation between sodium concentration c_{Na} and the stoichiometry ξ , $c_{\text{Na}} = (1 + \xi)/V_m$.

⁷ Introducing a ratio $\psi_{\text{el}} = u_{\text{e}'} / u_{\text{h}}$ of the electrical mobilities of the electronic charge carriers and normalising with the values at the stoichiometric point, $\sigma_{\text{e}^-}^{\#}$ and $\tilde{D}_{\text{Na}}^{\#}$, Eq. (44) and (45) can be simplified:

$$\frac{\sigma_{\text{e}^-}}{\sigma_{\text{e}^-}^{\#}} = \frac{\psi_{\text{el}}}{1 + \psi_{\text{el}}} \exp \operatorname{arsinh} \frac{\xi}{2\sqrt{K_{\text{el}}}} + \frac{1}{1 + \psi_{\text{el}}} \exp \operatorname{arsinh} - \frac{\xi}{2\sqrt{K_{\text{el}}}}$$

$$\frac{\tilde{D}_{\text{Na}}}{\tilde{D}_{\text{Na}}^{\#}} = 1 - \frac{1 - \psi_{\text{el}}}{1 + \psi_{\text{el}}} \tanh \operatorname{arsinh} \frac{\xi}{2\sqrt{K_{\text{el}}}}$$

3. Experimental setup

3.1. Material synthesis

All chemicals used in this synthesis were obtained from Sigma-Aldrich and used without further purification. Prussian White was synthesised via a co-precipitation method under Ar gas protection. Deionised water used in the synthesis was thoroughly degassed by Ar bubbling overnight [11]. For solution A, 6 mmol $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 25 mmol sodium citrate were dissolved in 100 ml of water. For solution B, 6 mmol $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ and 25 mmol sodium citrate were dissolved in 100 ml of water under continuous Ar purging. Solution A was stirred for 1 h at room temperature and then carefully added dropwise to solution B. The synthesis was performed at room temperature. After fully adding solution A, the mixture was continuously stirred over night to complete the reaction. The stirring speed was 600 rpm. Subsequently, an aging process of 24 h followed without stirring. The product was separated by centrifugation and washed with water (and again centrifuged) for three times. The wet product powder was dried at 80 °C by applying a vacuum at a base pressure of 10^{-2} mbar.

3.2. Materials characterisation

The morphology of the synthesised Prussian White powder was characterised by scanning electron microscopy (SEM, Zeiss Ultra plus) and Energy Dispersive X-ray Spectroscopy (EDX). The crystalline structure of the samples and the structural changing during the cycling were characterised by powder X-ray diffraction (XRD, Bragg–Brentano geometry, Bruker D8) using Cu-K_α radiation ($\lambda_{\text{Cu-K}_\alpha} = 1.5406 \text{ \AA}$). The refinement was performed by employing the software Profex3 (N. Döbelin, <https://www.profex-xrd.org>) [35]. Inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo Scientific) and thermogravimetric analysis (TGA, TA Instruments) were carried out to confirm the element concentrations and water content.

3.3. Cell setup

The cathodes (working electrodes, WE) were fabricated by manually doctor-blading an electrode slurry onto an aluminium foil. Prior to slurry preparation, the Prussian White powder was dried once again at 120 °C under vacuum (10^{-3} mbar). The slurry consisted of 70 wt% Prussian White powder, 20 wt% conductive carbon black and 10 wt% poly(vinylidene fluoride) (PVDF) as a binder. *N*-Methyl-2-pyrrolidone (NMP) served as a solvent to obtain the slurry. The resulting slurry was uniformly coated onto an aluminium foil and subsequently dried at 80 °C under argon atmosphere for 6 h to obtain the cathode material. The cathode was punched into a round shape (diameter 8 mm).

The coin cells (type 2032) for the coulometric titration measurements were assembled in an argon-filled glove box. Sodium metal was used as anode and a sintered NASICON disc as solid electrolyte separator. The NASICON ceramic material was supplied by the Institute of Materials and Devices (IMD-2), Forschungszentrum Jülich. Details of the materials synthesis are published elsewhere [36]. To improve the interfacial contact between cathode and NASICON, 5 μl of the liquid electrolyte 1 M NaPF_6 in EC/DEC were added.

The values at the stoichiometric point yield as:

$$\sigma_{\text{e}^-}^{\#} = \frac{F}{V_m} \sqrt{K_{\text{cl}}} (u_{\text{e}'} + u_{\text{h}}) \quad \text{and} \quad \tilde{D}_{\text{Na}}^{\#} = \frac{RT}{2F} (u_{\text{e}'} + u_{\text{h}})$$

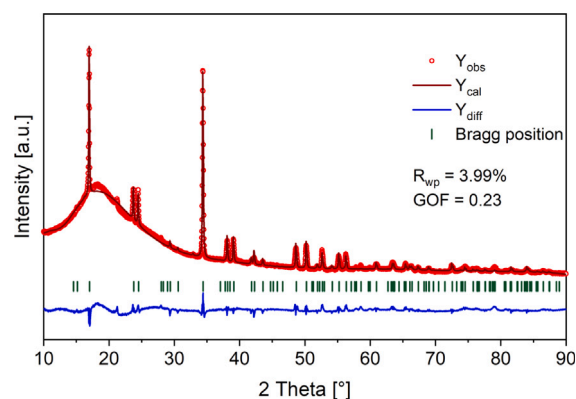


Fig. 5. XRD patterns and Rietveld refinement of PB powder.

3.4. Electrochemical measurements

Electrochemical measurements were carried out using a battery cycler system (Neware technology Ltd.). Prior to coulometric titration, the coin cells were activated for one cycle at a constant current density of 10 mA g^{-1} within a voltage window of 2.0–4.0 V. The change of the cell potential vs. time (charge) is recorded (quasi-stationary cell cycling).

To perform a coulometric titration in the same voltage window, the cells were charged and discharged with constant current pulses of 10 mA g^{-1} for 10 min per step, each followed by a 2 h rest period to measure the new equilibrium potential, i.e. using a galvanostatic intermittent technique (GITT). The obtained potential transients were evaluated to obtain the chemical diffusion coefficient of sodium.

4. Results

4.1. Elemental analysis and water content

According to the ICP-OES measurements, the nominal Na/Fe molar ratio of the Prussian White powder yields a value of 1.01 ± 0.01 , thus close to the ideal 1:1. TGA measurements after the first drying step (80 °C, 10^{-2} mbar) show a weight loss of 9.4 wt% below a temperature of 230 °C due to a release of the water. Based on this water content, the composition of the as-synthesised (initial) material is determined to be $\text{Na}_2\text{Fe}[\text{Fe}(\text{CN})_6] \cdot 1.81 \text{ H}_2\text{O}$. After an additional drying process at 120 °C under 10^{-3} mbar, the TGA results indicate a reduced water content of only 2.6 wt%, corresponding to a composition of approximately $\text{Na}_2\text{Fe}[\text{Fe}(\text{CN})_6] \cdot 0.46 \text{ H}_2\text{O}$.

4.2. Structural and morphological characterisation

The Prussian White powder refers as expected to a trigonal (rhombohedral) structure ($R\bar{3}c$), in accordance to the found high sodium content. The XRD pattern of the powder and the result of the refinement are depicted in Fig. 5. The lattice parameters are $a = b = 7.479(3) \text{ \AA}$, $c = 17.528(6) \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $V = 849.180(0) \text{ \AA}^3$ ($wR = 3.99$, $\text{GOF} = 0.23$). This indicates the presence of a trigonal phase with straight connected $\text{Fe}(\text{CN})_6$ octahedrons, see Fig. 2. The amorphous background is caused by a Kapton window to protect the sample against ambient humidity.

Using scanning electron microscopy (SEM), micrographs of the Prussian White powder are depicted in Fig. 6. A particle size distribution analysis yields an average size of about 10 μm . Using energy dispersive X-ray spectroscopy (EDX), the atomic ratio of Na to Fe was determined as approximately 1:1, which is consistent with ICP-OES result.

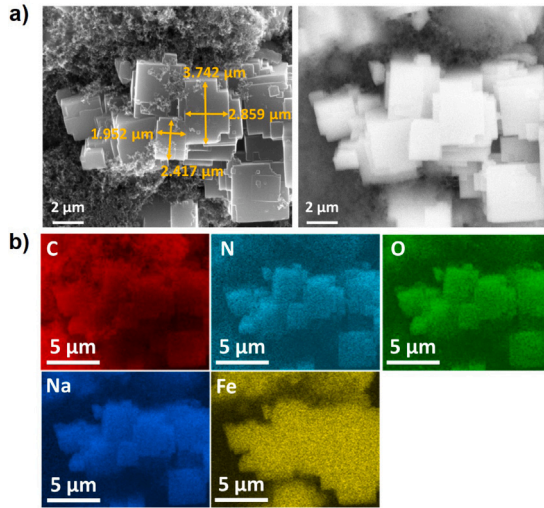


Fig. 6. (a) SEM images of PB-cathode, including secondary electron (SE) image and backscattered electron (BSE) image; (b) EDX elemental mapping analysis of PB cathode.

4.3. Coulometric intermittent titration

The coulometric intermittent titration (GITT) is started at maximum sodium content, respectively minimum cell potential. The change in stoichiometry $\Delta\xi$ is calculated by the time integral of the flown current according Eq. (33). The titration curve at $T = 298$ K is depicted in Fig. 7(a). The point of zero ($\xi = 0$) of the ξ -axis is set to the inflection point in the Prussian Blue phase, according to the results from fitting Eq. (34) to the data, see “Discussion”. The thermodynamic factor is calculated according Eq. (37) and depicted in Fig. 7(b).

At a cell Potential U_{cell} of 3.7 V a stoichiometry ξ of -0.8 is reached. This corresponds to a composition of $\text{Na}_{0.2}\text{Fe}[\text{Fe}(\text{CN})_6]$ and a capacity q_{max} of 152 mAh g^{-1} .⁸

4.4. Quasi-stationary cell cycling

The results from the first cycling at a constant current density of 10 mA g^{-1} in a voltage window of 2.0–4.0 V is supplied in the supplemental material (III). The change in stoichiometry ξ is calculated according Eq. (33).

4.5. Chemical diffusion coefficient of sodium

According Weppner and Huggins, the chemical diffusion coefficient $\tilde{D}_{\text{Na}}$ of sodium in Prussian Blue can be obtained at each GITT step by analysing the cell potential transients and considering the thickness of the whole electrode as characteristic diffusion length [37]. However, in the case of composite electrodes, consisting of an active material, conductive carbon and a binder, this will lead to wrong results as the rate limiting diffusion process may occur only in the particles of the active material and not in the whole composite structure. According Nickol et al. and Schied et al. this results in following modified equation: [38,39]

$$\tilde{D}_{\text{Na}} = \frac{4}{\pi\tau} \left(\frac{r_p}{3} \right)^2 \left(\frac{\Delta U_{\text{cell},s}}{\Delta U_{\text{cell},t}} \right)^2 \quad (46)$$

⁸ The actual capacity q_{max} can be calculated from the ideal capacity 168.68 mA g^{-1} and the accessible minimum sodium content/stoichiometry ξ_{min} , as the fully sodiated compound $\text{Na}_2\text{Fe}[\text{Fe}(\text{CN})_6]$ exists:

$$q_{\text{max}} = 168.68 \text{ mA g}^{-1} \cdot \frac{1 - \xi_{\text{min}}}{2}$$

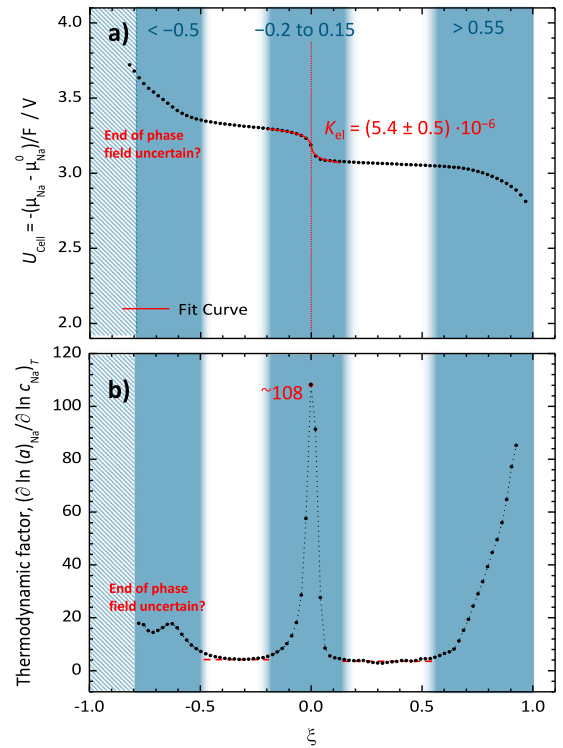


Fig. 7. (a) Coulometric titration, i.e. cell voltage U_{cell} vs. ξ , fit of Eq. (34) to the data (red solid line). (b) Thermodynamic factor $(\partial \ln a_{\text{Na}} / \partial \ln c_{\text{Na}})_T$ vs. ξ . The ξ -axes in (a) and (b) are shifted to adjust $\xi = 0$ to the inflection point. Tentative boundaries of single phase fields are marked by shaded areas (Prussian white: right, Prussian blue: middle, Prussian yellow: left).

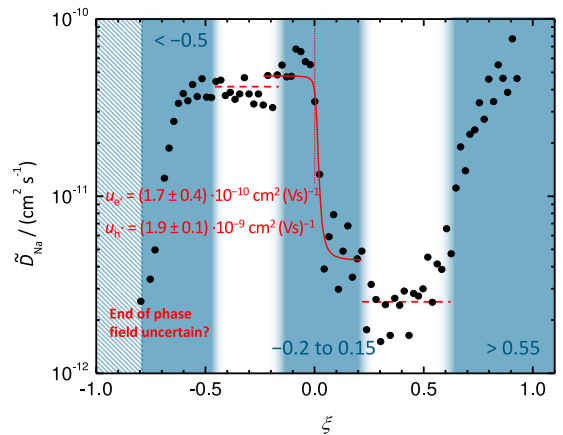


Fig. 8. Chemical diffusion coefficient $\tilde{D}_{\text{Na}}$ vs. ξ . Fit of Eq. (45) to the data (red solid line). The ξ -axis is shifted to set the inflection point of the coulometric titration data to $\xi = 0$. Tentative boundaries of single phase fields are marked by shaded areas (Prussian white: right, Prussian blue: middle, Prussian yellow: left).

Hereby, τ is the duration of a current pulse and r_p the average particle radius of the active material. Considering the results from the SEM investigations, an average radius of $5 \mu\text{m}$ for the Prussian Blue particles is used. The voltage variation after a coulometric titration step, i.e. applying a constant current pulse and waiting for a new equilibrium potential, is denoted as $\Delta U_{\text{cell},s}$ and the change of the cell voltage during the constant current pulse as $\Delta U_{\text{cell},t}$.

The measured chemical diffusion coefficient $\tilde{D}_{\text{Na}}$ of sodium is plotted vs. ξ , see Fig. 8. ξ is calculated from the cell potential U_{cell} by using

8

The energy E_{IT} of the optical excited intervalence charge transfer from the t_{2g} -state of Fe_{LS}^X to the t_{2g} -state of Fe_{HS}^X has a value of 1.75 eV and can be assigned as band gap of Prussian Blue [44,45]. Optically excited and radiationless electronic transfers in mixed valence inorganic compounds with complex ligands, as present in the Prussian Blue, can be treated by Marcus-Hush theory [46]. In a semi-classical description, two localised electronic states are assumed. In the initial state, $Fe_{LS}^{2+}-CN-Fe_{HS}^{3+}$, the difference of the nuclear coordinates of the iron ions is denoted with q_{is} . In the final state, $Fe_{LS}^{3+}-CN-Fe_{HS}^{2+}$, the difference is denoted with q_{fs} . The Gibbs free enthalpy of these states G_{is} and G_{fs} vs. the deviation from the equilibrium position due to thermal excitation is simply described by harmonic potentials, see Fig. 9 and also Liu and Meng [47]. The vibrational motion of the iron ions is described as harmonic oscillator. The same force constant f is assumed for both harmonic potentials:

$$G_{is} = \frac{f}{2} (q - q_{is})^2 \quad (49)$$

$$G_{fs} = \frac{f}{2} (q - q_{fs})^2 + \Delta G_{el}^0 \quad (50)$$

The Gibbs free enthalpy difference between initial and final state, each in the vibrational ground state, should be equal to ΔG_{el}^0 .

Due to Franck-Condon principle, an optical intervalence transfer in Fig. 9 will occur on a path along arrow (a). An energy of E_{IT} has to be overcome. Subsequently, the system is in an excited vibration mode and will relax after dissipation of the reorganisation energy λ .

The vibrational modes in the initial state are occupied according to the Boltzmann distribution. In the case of a radiationless, thermally excited transition, the electron transfer will take place when the system overcomes the barrier $\Delta G_{el}^\#$, see the path along arrow (b) in Fig. 9. The following relations result:

$$\lambda = \frac{f}{2} (q_{fs} - q_{is})^2 \quad \text{and} \quad E_{IT} = \lambda + \Delta G_{el}^0$$

$$\Delta G_{el}^\# = \frac{(\lambda + \Delta G_{el}^0)^2}{4\lambda} = \frac{E_{IT}^2}{4(E_{IT} - \Delta G_{el}^0)} \quad (51)$$

The barrier $\Delta G_{el}^\#$ of the thermally activated intervalence electron transfer is related to the activation energy $E_{a,el}$ of the electronic partial conductivity σ_{e-} . Considering $E_{opt} = 1.75$ eV, the value of $\Delta G_{el}^0 \approx 0.31$ eV and Eq. (51), yields a value of $\Delta G_{el}^\# \approx 0.53$ eV. In a recent publication, Navar and Alzarani supply a value of 0.565 eV, which is in remarkably good accordance.⁹

5.4. Chemical diffusion coefficient of sodium

Within the estimated phase field of Prussian Blue, the course of the chemical diffusion coefficient $\tilde{D}_{Na}$ vs. ξ exhibits the expected “step-like” behaviour in the vicinity of the stoichiometric composition ($\xi = 0$) and is changing from $5 \cdot 10^{-11}$ to $3 \cdot 10^{-12}$ cm² s⁻¹, see Fig. 8. In the adjacent two-phase fields, its value is nearly constant. In the Prussian White and Prussian Yellow phase field, $\tilde{D}_{Na}$ is increasing with increasing ξ .

The measured values of $\tilde{D}_{Na}$ are in the lower range of the values supplied by the literature (see supplemental material VI) [8,22,49–53]. Komayko et al. also address the problem choosing the characteristic diffusion length when performing electrochemical transient measurements like GITT on Prussian Blue composite electrodes [54]. Depending on the electronic partial conductivity of the active material, the distribution of the conductive carbon and the binder, the diffusion length may not be identical to the layer thickness but to the dimensions of the carbon

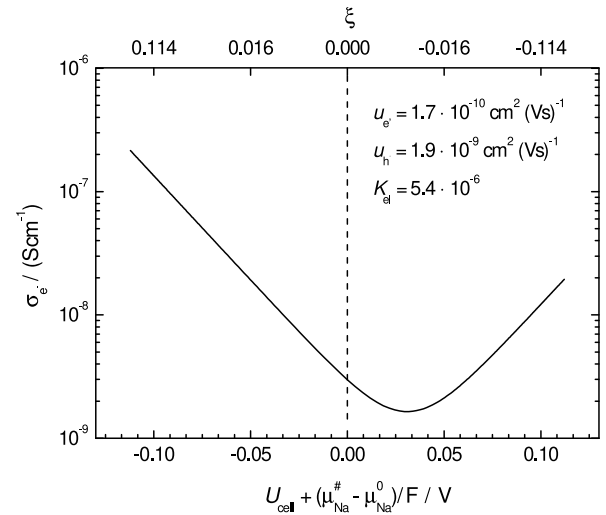


Fig. 10. Calculated electronic conductivity σ_{e-} vs. cell potential $U_{cell} + (\mu_{Na}^\# - \mu_{Na}^0)/F$, using the values found for u_{e-} , u_{h-} and K_{el} . Upper axis scaled against the stoichiometric deviation ξ .

coated particles of the active material. This would lower the calculated value for $\tilde{D}_{Na}$ by 2–3 orders of magnitude.

Eq. (45) can be used to fit the diffusion data in the Prussian Blue phase according to the point defect model. This yields values for the electrical mobilities u_{e-} and u_{h-} of “electron” and “holes” of $(1.7 \pm 0.4) \cdot 10^{-10}$ and $(1.9 \pm 0.1) \cdot 10^{-9}$ cm² (Vs)⁻¹. Such low values indicate a very strong, nearly insulator-like localisation of the charge carriers and support the presence of small polarons. Remarkably, the mobility of “holes” is about one order of magnitude higher compared to “electrons”.

Mobilities in the order of 10^{-3} cm² (Vs)⁻¹ are found in simple binary metal oxides with electronic conduction based on small polarons, e.g. MnO and CeO₂ [55,56]. However, LiFePO₄, a compound with a complex anion, features even lower mobilities. According to the hopping frequency and distance, the mobility of its “hole” polarons is in the order of 10^{-6} cm² (Vs)⁻¹ [57,58]. The electronic charge transport in Prussian Blue is more comparable to this material.

The inflection point, determined by fitting the diffusion data, does only deviate by $\Delta\xi = 0.04$ from the inflection point determined by fitting the coulometric titration data. For K_{el} a value of $(4.6 \pm 4.9) \cdot 10^{-5}$ is obtained, significantly higher compared to the results from coulometric titration. However, it is not very reliable due to the higher scattering of the diffusion data.

5.5. Electronic partial conductivity

The electronic partial conductivity σ_{e-} of Prussian Blue can be calculated using the values found for u_{e-} , u_{h-} and K_{el} as well as V_m and Eq. (44). The functional course of σ_{e-} vs. cell potential $U_{cell} + (\mu_{Na}^\# - \mu_{Na}^0)/F$ relative to the stoichiometric composition, features a characteristic v-shape and a minimum close to the stoichiometric point, see Fig. 10. The minimum is shifted to positive values as the mobility u_{h-} is higher than u_{e-} . This corresponds to positive deviations from stoichiometry ξ . However, systematic measurements of σ_{e-} as a function of U_{cell} or ξ are not available in literature.

The calculated values for σ_{e-} are in the range between 10^{-7} to 10^{-9} S cm⁻¹. This is in the same order of magnitude as the values found in literature (see supplemental material V) [4,27,30–32]. This indicates that the average radius of the active material particles is the right choice for the characteristic diffusion length to obtain reliable values for $\tilde{D}_{Na}$ and suggests an overestimation by many recent studies.

⁹ $\Delta G_{el}^\#$ consist of an enthalpic and an entropic contribution, i.e. $\Delta G_{el}^\# = \Delta H_{el}^\# - T\Delta S_{el}^\#$. The activation enthalpy $\Delta H_{el}^\#$ is (nearly) equal to the activation energy $E_{a,el}$, as in a solid the volume change can be neglected. The entropic contribution $T\Delta S_{el}^\#$ is usually small (typically ~ 1.7 kJ mol⁻¹ or ~ 0.02 eV at room temperature) [48].

6. Conclusions

The quasi-binary system Na–Fe(CN)₃ is investigated by galvanostatic intermittent coulometric titration (GITT) to gain thermodynamic data and the chemical diffusion coefficient of sodium. Point defect thermodynamics based on C. Wagner and F. A. Kröger is applied to describe the Prussian Blue phase Na_{1+ ξ} Fe[Fe(CN)₆]. The stoichiometry ξ dependent molar fractions of the defect species Fe^{II}_{HS} and Fe^{III}_{LS} are decisive for the electrochemical properties. They can be identified as “electron” and “hole”, i.e. as minority defects.

Expressions to describe the titration curve U_{cell} vs. ξ and the course of the chemical diffusion coefficient $\bar{D}_{\text{Na}}$ vs. ξ are derived on the basis of the model and successfully proven by fitting the experimental data. The titration curve U_{cell} vs. ξ and the chemical diffusion coefficient $\bar{D}_{\text{Na}}$ exhibit characteristic S-shaped courses due to the thermal equilibrium of the minority defects. An inflection point marks the stoichiometric composition $\xi = 0$. The equilibrium constant K_{el} for the thermally induced formation of the minority defects, the defect concentrations, the Gibbs free formation enthalpy ΔG_{el}^0 and the electrical mobilities $u_{\text{e'}}$ and $u_{\text{h'}}$ of the minority defect are obtained from the fitting process.

The found Gibbs free formation enthalpy ΔG_{el}^0 can be related according Marcus-Hush theory to the optical intervalence transfer energy (band-gap) and the activation energy of the electronic partial conductivity obtained from literature. The electrical mobilities $u_{\text{e'}}$ and $u_{\text{h'}}$ are decidedly small and clearly indicate the presence of small polarons due to a strong localisation.

The localisation of the stoichiometric composition at the inflection point clearly supports the existence of a fully sodiated trigonal phase, Na₂Fe[Fe(CN)₆]. However, according to the observed course of the titration curve the existence of a fully de-sodiated phase, Fe(CN)₃, seems to be unlikely. The point defect model allows an estimation of the electronic partial conductivity $\sigma_{\text{e'}}$ using diffusion data. It should feature a v-shaped dependency on ξ with a minimum in the vicinity to the stoichiometric composition.

CRedit authorship contribution statement

Carsten Korte: Writing – original draft, Supervision, Investigation, Formal analysis, Conceptualization. **Ying Hu:** Writing – review & editing, Investigation. **Piotr Kowalski:** Writing – review & editing, Investigation. **Changchun Jo:** Writing – review & editing. **Christian Rodenbücher:** Writing – review & editing. **Sangwon Kim:** Writing – review & editing. **Jungtae Kim:** Writing – review & editing.

Declaration of competing interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.ssi.2026.117336>.

Data availability

Data will be made available on request.

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