

Batteries & Supercaps

Supporting Information

Rhombohedral ($R\bar{3}$) Prussian White as Cathode Material: An *Ab-initio* Study

Sebastian Baumgart,* Mohsen Sotoudeh, and Axel Groß*

Supplementary Discussion: The failure of GGA+U

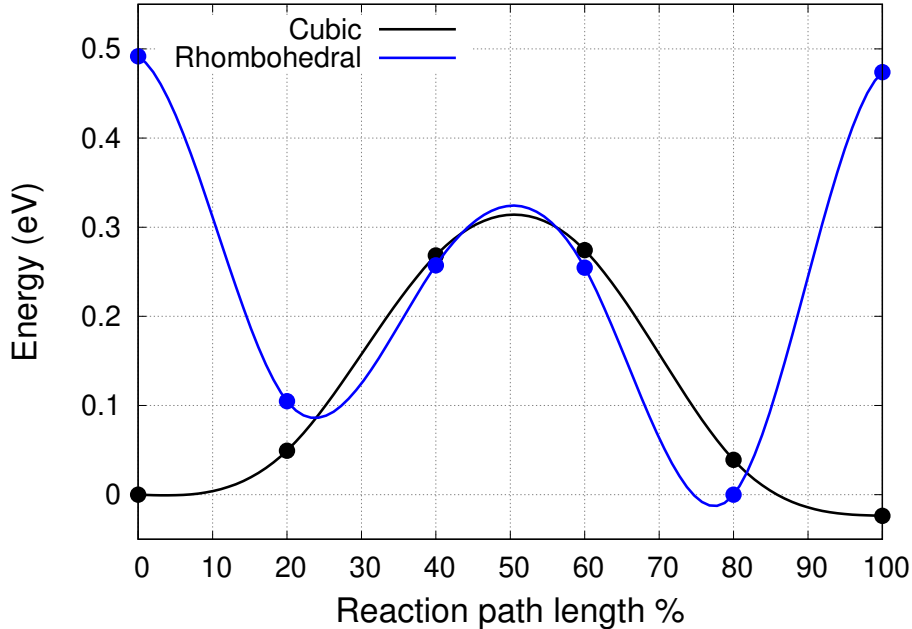


Figure S1: Erroneous Na migration energy barriers (in eV) as a function of the reaction path coordinate derived from periodic DFT calculations combined with NEB for the single-ion migration from the initial site to the next nearest neighboring site corresponding to the $\text{Na}_2\text{Fe}[\text{Fe}(\text{CN})_6]$ PW with the rhombohedral crystal structure (blue color). The minimum energy path for the cubic crystal structure (black color) is included for comparison. The minimum energy is set to zero.

During the planning stage of this project, the idea was to keep using GGA+U during the NEB calculations, despite accounts being known to the authors that talked about a reduced convergence stability of NEB calculations when utilizing this method in combination with the Hubbard U-correction. A deciding factor for this decision was the interconnection of electronic structure and atomic geometry in this specific material, i.e. a U-parameter that is selected by fitting the band gap of the material does also restore the hs-ls spin state as the calculated ground state. The change from a ls-ls- to a hsls-spin state also changes the lattice constant of the material by $\sim 0.4 \text{ \AA}$. Therefore it is not only electronically, but also geometrically advantageous to use GGA+U for this material.¹ When using the GGA+U functional for the NEBs, we encountered artificially stabilized images along the sodium migration path,

leading to a W shaped energy profile. When then using the "new" minimum energy geometries of these images within a geometry optimization (or anything else except an NEB) they revert back to the previous optimized structures, indicating an addition of energy into the system by an artificial over-localization of charge caused by the U -correction during the NEB. As the interference of the U -parameter with NEB calculations is already known in literature,^{2,3} we decided to progress by using the GGA+U geometries as an input for a GGA only NEB calculations. Hybrid functionals could be utilized as well, however, they have a well-known drawback: utilizing hybrid functionals significantly increases the computational expenses associated with NEB calculations, making them more time-consuming and expensive. Consequently, it is typically recommended to opt for non-hybrid density functionals like GGA or meta-GGA functionals for NEB calculations. These functionals are less demanding in terms of computational resources, provide accurate results for most systems, and have undergone extensive validation for a wide range of applications. More recent benchmarking efforts have revealed that the meta-GGA (SCAN) framework is generally more accurate than other functionals, although it does come with higher computational costs and issues related to convergence.² In contrast, GGA remains a viable choice for quick and qualitative predictions of migration barriers.

Lastly, this problem seems to also interfere with the correct determination of intercalation voltages, resulting in unphysically low voltages for cubic and rhombohedral PW. Therefore these values also had to be determined with the GGA-functional on GGA+U geometries to yield reasonable values.

Additional visualizations of the phase transformation

Figure S2 offers alternative visualizations of crystal structures presented in the main text. In (a) the rhombohedral cell is viewed along the $\text{Fe}^{2+}-\text{CN}-\text{Fe}^{2+}$ bond, matched to the conventional unit cell of the cubic system, which is depicted in (b). (c) displays the rhombohedral

unit cell in a $3 \times 3 \times 1$ supercell view along the a-axis. Matching to this depiction, (d) shows the $2 \times 2 \times 2$ supercell of the cubic phase placed onto its vertex.

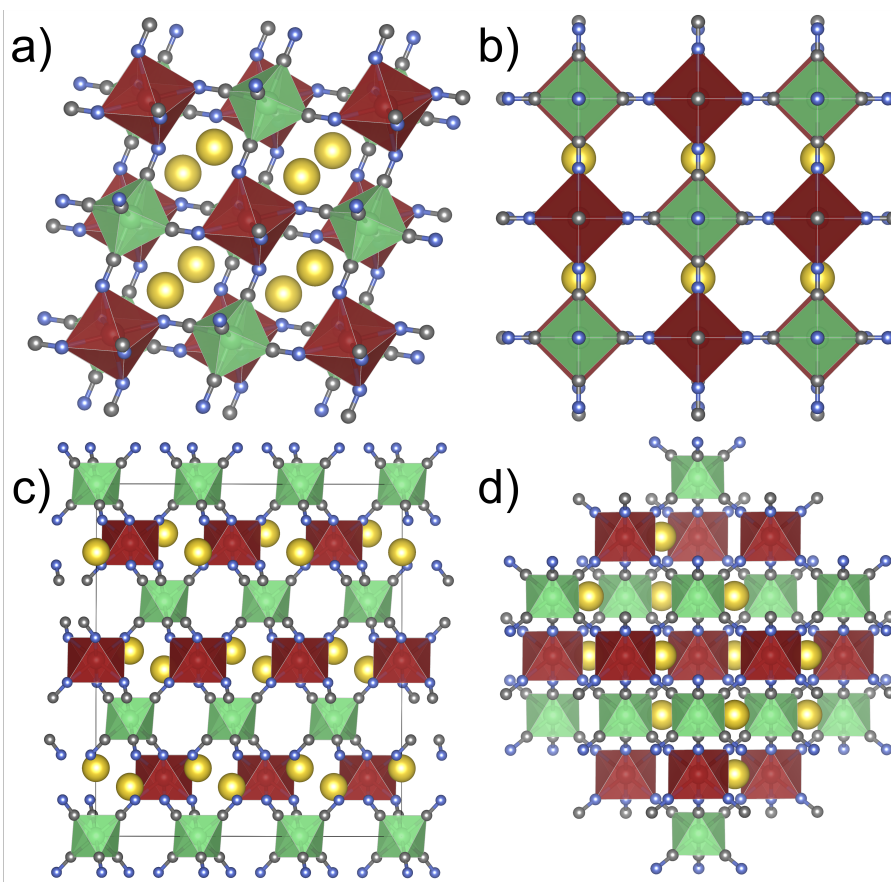


Figure S2: Alternative visualizations of the crystal structures of rhombohedral and cubic Prussian White. In these structures, the high-spin transition-metal ion is represented by a red sphere, the low-spin transition-metal ion is represented by a green sphere. Coordination polyhedra were made slightly transparent and are colored in accordance with the color of their central atom. The nitrogen atoms are represented by a blue sphere, the carbon atoms by a grey sphere, and sodium atoms by yellow sphere.

Available interstitial positions in C-PW

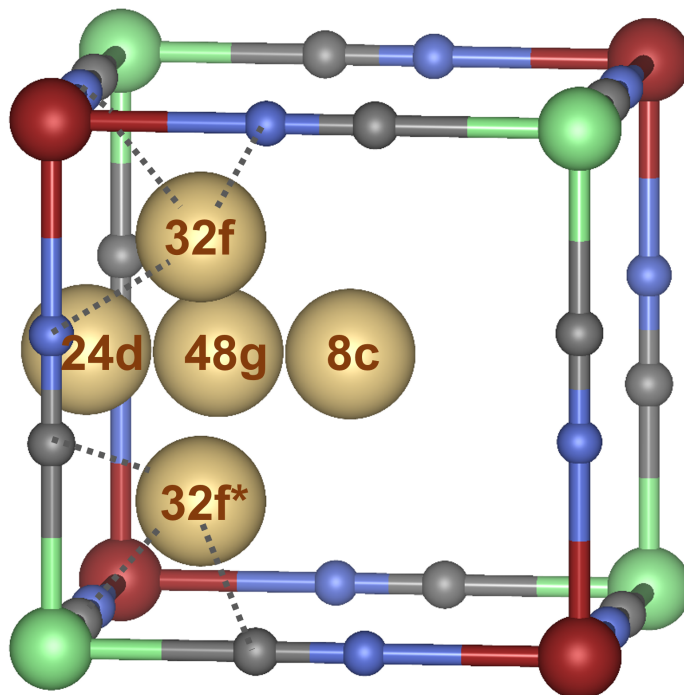


Figure S3: A section of the crystal structure of C-PW is depicted to illustrate the five potential interstitial spaces within the framework.

Figure S3 depicts the 5 potentially available crystallographic interstitial sites within the C-PW structure: 8c (body-centered), 24d (face-centered), 32f (shifted from 8c locations towards the N-coordinated corner), and 32f* (shifted from 8c locations towards the C-coordinated corner) and 48g (halfway between 24d and 8c).

Additionally, Table S1 contains a more detailed structural comparison for a two possibilities for the Prussian White structure. Labeled with "Fcc" is a structure of C-PW, in which all sodium cations occupy a face centered site (Wyckoff: 24d), while the label "Bcc" marks a structure in which all sodium atoms were shifted to the body-centered void (Wyckoff: 8c) of their respective cube. It can be seen that the Bcc-structure is destabilized by 141 meV per atom, when compared the the Fcc variant, showing just how strongly sodium favors the face centered site. Furthermore, the occupation of the face centered sites by sodium leads to a small increase in the lattice constant of the Prussian white compound, which is mostly

compensated by stretching the Fe-N bond. This again proves the low flexibility of the Fe-C bond, when compared to the Fe-N bond.

Table S1: Structural comparison of cubic ($Fm\bar{3}m$) Prussian white with sodium ions occupying different interstitial positions within the lattice. Highlighted in bold font is the most stable configuration.

Property	Fcc	Bcc
Relative energy per atom [eV]	0.00	0.141
lattice constant [\AA]	10.498	10.353
V [\AA^3]	1156.96	1109.53
d($\text{Fe}_{\text{ls}}^{2+}$ -C) [\AA]	1.878	1.883
d(C-N) [\AA]	1.181	1.181
d($\text{Fe}_{\text{hs}}^{2+}$ -N) [\AA]	2.190	2.113
d($\text{Fe}_{\text{ls}}^{2+}$ - $\text{Fe}_{\text{hs}}^{2+}$) [\AA]	5.249	5.176

Geometric observations on the Fe-CN-Fe square in cubic and rhombohedral Prussian white

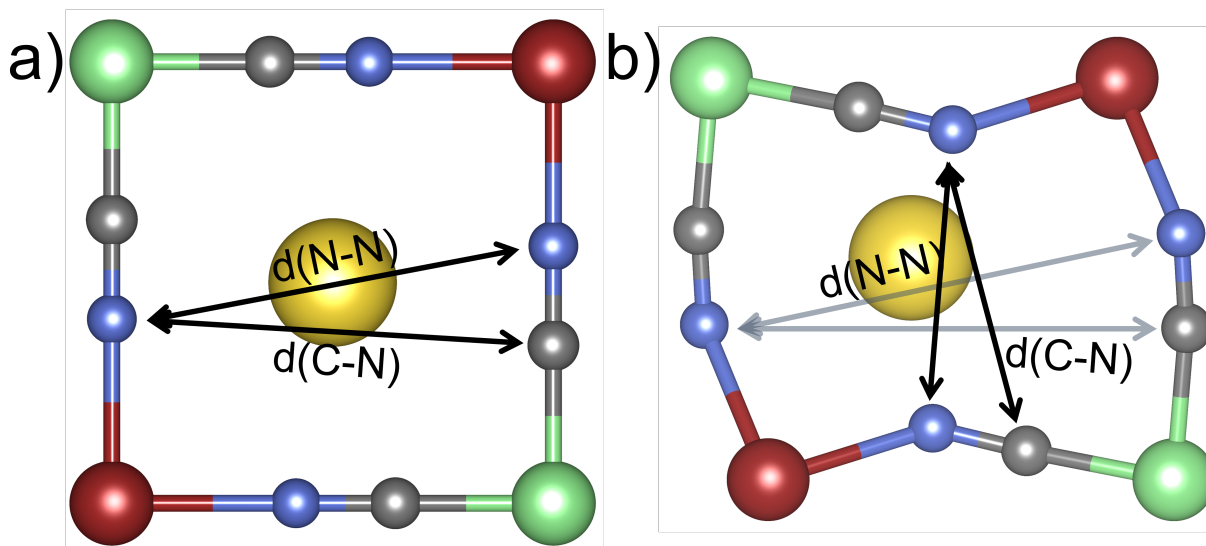


Figure S4: Clean visualization of the Fe-CN-Fe square, representing the fcc plane in cubic and rhombohedral Prussian white, and the evaluated distances.

Figure S4 depicts the geometrical factors for the evaluation of the site volume used. While the sodium in the image of C-PW (Figure S4 left) is positioned within the plane spanned by

the surrounding atoms, the sodium in the rhombohedral PW phase (right) is positioned in its minimum energy position behind the plane of the remaining atoms. The measured distances are summarized in Table S2. Due to the asymmetric distortion in the rhombohedral system, the formerly equidistant sides of the square are distorted as well, resulting in one stretched and one compressed distance. Both are given with the percentile change with respect to the same distance in the cubic PW phase.

Table S2: Structural comparison of the Wyckoff position 24d in cubic and rhombohedral Prussian white. The listed distances are visualized in the above depiction. Percentages given in parenthesis are relative to the respective cubic PW value.

Property	C-PW	R-PW
d(C-N) [\AA]	5.254	4.113 (-21.7%)
	–	5.977 (+13.7%)
d(N-N) [\AA]	5.332	3.788 (-29.0%)
	–	6.065 (+13.7%)

DOS of cubic Prussian white

The calculated DOS of the cubic Prussian White modification is given in Figure S5. The main difference is the smaller energetic separation of the states observed between -6 and 6 eV. The shift of DOS around the Fermi level shows the influence of the octahedron tilting on the electronic properties. Furthermore, the DOS is influenced by the a_{1g} - and e'_g -states merging back together to reform the t_{2g} -states during the rhombohedral/cubic phase transition.

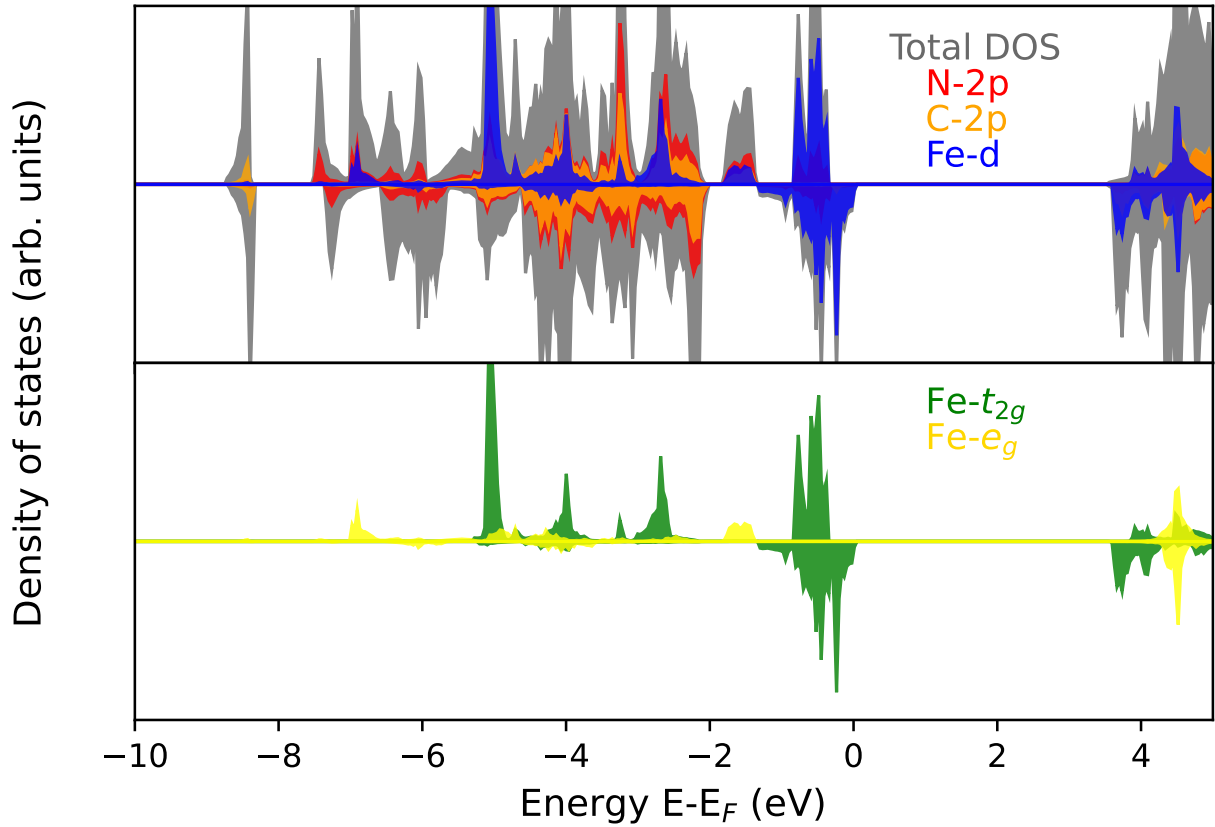


Figure S5: The calculated electronic density of states (DOS) for the cubic Prussian White phase. The total DOS is given in grey in the top graph. The projected DOS are shown in blue for Fe- d states, in red for N- $2p$ states, in orange for C- $2p$ states. The Fermi energy is shifted to 0 eV. Majority spin states are plotted upwards, minority spin downwards. The bottom graph shows the orbital decomposed Fe- d states, namely t_{2g} - (green) and e_g -orbitals (yellow).

References

- (1) J. C. Wojdel, S. T. Bromley, *J. Phys. Chem. B* **2006**, *110*, 24294–24298.
- (2) R. Devi, B. Singh, P. Canepa, G. Sai Gautam, *Npj Comput. Mater.* **2022**, *8*, 160.
- (3) M. Sotoudeh, M. Dillenz, J. Döhn, J. Hansen, S. Dsoke, A. Groß, *Chem. Mater.* **2023**, *35*, 4786–4797.