

Phases of Prussian Blue Analogue Cathodes

Jake Bilyk

UC San Diego

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Author Notes:

Best wishes to all the humans pursuing battery chemistries that will enable electrical utility access for all people on earth. There is absurd abundance in the earth's materials if they are harvested appropriately.

The figures within this document belong to the authors listed in the references. The report frequently refers to the experimental work of Qin-Fen Gu, Shu-Lei Chou et al. (2020, 2022)^{1,2}. Theoretical data presented in this paper was sourced from Shuye Ping Ong et al. (2019)³.

Abstract

The purpose of this paper is to strengthen my understanding of phase transitions within the active materials (cathodes specifically) of Prussian Blue Analogue (PBA) based batteries. The coordinated cathode material prefers specific crystal geometries depending on the voltage of the cell and the chemical activity of the water content. In other words, the phase of the PBA is dependent on the alkali-ion concentration and water coordination in the lattice. The papers published by Chou S-L, Gu Q-F, et al in *Nature Communications* and *Wiley Advanced Materials* demonstrate significant insight into highly desirable battery synthesis/characterization techniques. An excellent numerical based publication that compliments these papers was written by UC San Diego Professor Dr. Shyue Ping Ong et. al which generated thermodynamic data related to PBA water content and Na^+ concentration. In some cases, the theoretical data matched very well with historical empirical data. If major breakthroughs are made in these PBA chemistries, then the world will have a much better chance of reaching energy storage needs for a cooler future. Sodium, iron, aluminum, and cyanometallates are all very abundant and affordable compounds. Scientists and engineers are currently optimizing this desirable recipe for stationary energy storage batteries!

Introduction

For clarity, let us establish the exact material of interest. Prussian Blue is a coordination compound discovered in the 1700s by a painter in Berlin, Germany⁴. It has the chemical formula $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$. The first publication demonstrating its behavior in an electrochemical cell was written by chemist Vernon Neff in 1978. The term Prussian Blue Analogue (PBA) refers to similar coordination structures with varying cation substitution (Fe^{2+} , Fe^{3+} can be exchanged for other transition metal elements). This type of nomenclature is comparable to the way scientists

refer to diverse types of Perovskite structures. Regarding sodium-ion batteries, PBAs assume the general formula $\text{Na}_{2-x}\text{M}[\text{Fe}(\text{CN})_6]_{1-y}\square_y \cdot n\text{H}_2\text{O}$ where M is an alternative divalent metal, \square is a vacancy that can be filled by a chelated water molecule, and y is number of filled vacancies. PBAs are becoming increasingly attractive for use as battery active materials because of their low cost and strong cycling performance.

Chou S-L, Gu Q-F, et al discussed some of the previously studied materials and highlighted the attractiveness of $\text{Na}_{2-x}\text{MnFe}(\text{CN})_6$ after Goodenough's lab demonstrated quality performance in 2013. Realizing that the presence of Mn cations in the lattice can lead to higher probability of negative structural consequences (Jahn-teller effect distortion), the team decided to focus their efforts on optimizing a Prussian White (PW) cathode $\text{Na}_{2-x}\text{FeFe}(\text{CN})_6$. They also identified the known failure mechanism of the cathode material they intended to study; below in Figure 1, the three reversible phases of PW can be visualized. Technically, the term PW refers to the fully sodiated structure: $\text{Na}_2\text{FeFe}(\text{CN})_6$, but the name can also be used generally to describe the cathode active materials. If the sodium content in the cubic/tetragonal phase is too low and the crystal environment lacks coordinated water, the structure can be reduced and locked in cubic phase that impedes Na^+ ion flow. Here, the purple tetrahedrons represent Fe centers bound to

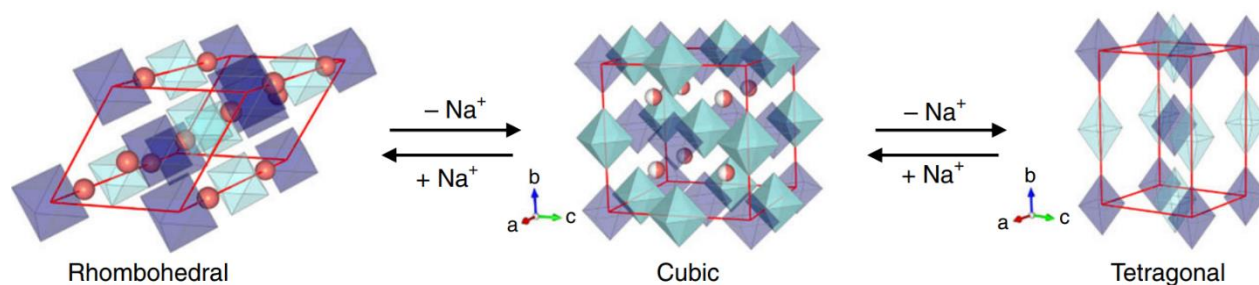


Figure 1

carbon atoms and the blue represent Fe centers bound to the nitrogen atoms of the cyanate groups. The red atoms represent sodium. Notice in the cubic structure, the sodium ions are half

white, representing the varying concentrations. Although the rhombohedral and cubic phases are generally more stable, certain conditions discussed later allow for improved cell performance in the tetragonal phase as well.

In search of a thermodynamic approach for characterizing the electrochemical behavior of the PW material, I was excited to see that UCSD helped publish exactly what I wanted to convey in this portion of the report. Utilizing ab initio simulation software, Ong et al. calculated the Grand potential diagrams for many PBAs and below in Figure 2 is the calculated phase diagram for $\text{Na}_{2-x}\text{FeFe}(\text{CN})_6$ systems. At the bottom left coordinate of the graph $(-4, 10^{-10})$, the phase diagram represents the absence of sodium and water in the lattice in the tetragonal phase.

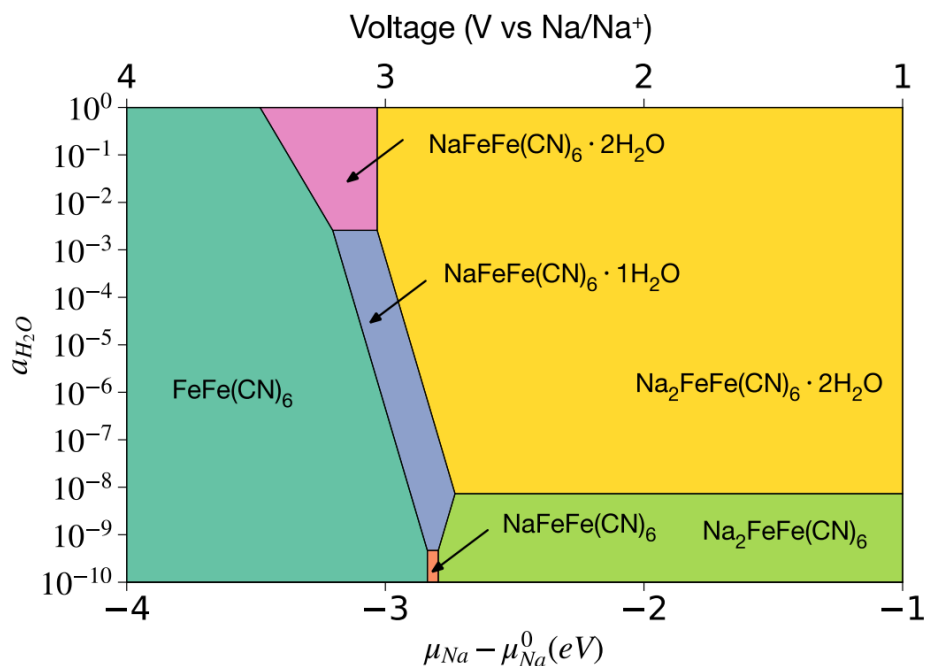


Figure 2

The electrochemical cell can operate across nearly all the phases, still it is important to avoid conditions that may affect the reversibility/efficiency of the process and understand which divalent metal can provide the best combination of stability and voltage. I am particularly interested in the FeFe arrangement because it is the most economic choice. However, by

comparing phase diagrams across the choices of M in $\text{Na}_{2-x}\text{M}[\text{Fe}(\text{CN})_6]_{1-y}\cdot n\text{H}_2\text{O}$, $\text{NaFeFe}(\text{CN})_6 \cdot 1\text{H}_2\text{O}$ (purple/blue area) and a tiny $\text{NaFeFe}(\text{CN})_6$ dehydrated phase area (orange). Other cation combinations may deliver better voltage profiles because of wider phase stability ranges, one of many reasons why the thermodynamic data can be critical for active materials selection. Hypothetically, assume one has a PW cathode operating in the voltage range from 2 – 4 V. If the material is very dry, it must experience two quick phase changes around 2.8 V. The thermodynamics of this process become very relevant to the performance, and we will see later how the calculated formation energies can provide insight into which PBAs may be most thermodynamically viable for practical use.

Strategy

First, the strategies and goals of the experimentalists (Chou S-L, Gu Q-F, et al) will be summarized. As with many industries, uniformity and consistency are key to product success. For this reason, it is extremely important for battery scientists to identify methods that lead to the most reproducible and best performing active materials. For PBAs to succeed, uniform nucleation of the crystals is required during the co-precipitation synthesis. Gu et. al synthesized a strategic series of $\text{Na}_{2-x}\text{FeFe}(\text{CN})_6$ slurries with varying values of ‘x’ and different sodium citrate addition methods. The recipe they used was cited as an adaptation of previously published PBA syntheses from 2016. The team commented on the significance of sodium citrate addition techniques and the effects on particle growth. The author’s recipe suggests that sodium citrate be added in both FeSO_4 and $\text{Na}_4\text{Fe}(\text{CN})_6$ solution reagents and in the proper amounts. An ideal synthesis produces a uniform population of microcubes, and the authors demonstrated a quality yield of $\sim 1\mu\text{m}$ edge-length cubes seen below in Figure 3 g, h. for their electrochemical cell test

materials. This team built an impressive cell nearly making the 80 % efficiency retention mark for 1000 cycles. Commercial laboratories are producing similar batteries with higher retention⁵.

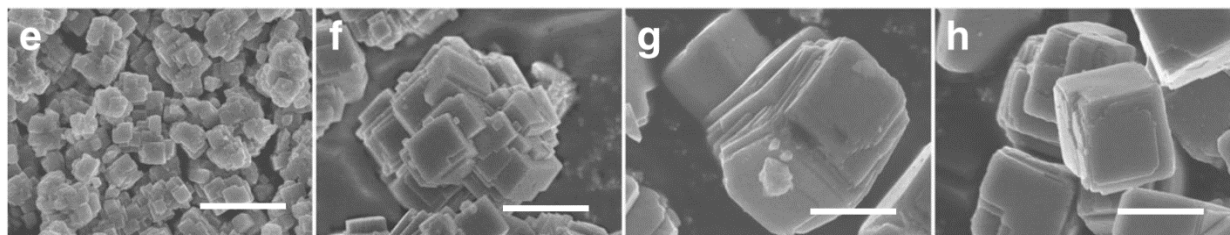


Figure 3

The computational strategy employed by Ong et. al involved a series of steps intended to calculate the theoretical voltage, chemical potential (μ_{Na} , $\mu_{\text{H}_2\text{O}}$) and chemical activity of the species of interest. My computational chemistry skills are limited to using Hartree-Fock method in Spartan software ~10 years ago to calculate orbital energies in small organic molecules, so I am not able to thoroughly describe the approach taken by the team. Still, the thermodynamic principles are apparent; the Gibbs free energy term (G) seen below is composed of the energy of formation (enthalpy) and lattice entropy values calculated by the *Vienna Ab Initio Simulation Package* with the teams input parameters. The parameters are chosen from NIST databases

$$\Phi = \frac{G_{\text{Na}_x\text{P}[\text{R}(\text{CN})_6] \cdot n_{\text{H}_2\text{O}} - n_{\text{H}_2\text{O}}\mu_{\text{H}_2\text{O}} - n_{\text{Na}}\mu_{\text{Na}}}{e} \quad V = -\frac{\mu_{\text{Na}} - \mu_{\text{Na}}^0}{e}$$

$$\mu_{\text{H}_2\text{O}(l)} = \mu_{\text{H}_2\text{O}(l)}^0 + RT \ln a_{\text{H}_2\text{O}(l)}$$

and other reputable sources. The goal is applying these equations with the assistance of massive computing power. The team specified that the mesh they were using accounted for a minimum of 1,000 k-points per number of atoms in the unit cell. For those that know a little bit about reciprocal space, one can imagine why the team cited the use of three different computing facilities (TSCC, NERSC, XSEDE). Later we will discuss how the Heyd–Scuseria –Ernzerhof functional (HSE) can be used to characterize stable phases by calculating formation energies.

Discussion

Honestly, this was the first time I have seen the PXRD curves as heat maps and surface-like plots. The figures in these papers are the features I enjoy the most as they are beautifully done. The image that I stared at for a long time is below in Figure 4. So much information can be inferred by plotting a combination of contoured XRD phases, with voltage and cycling.

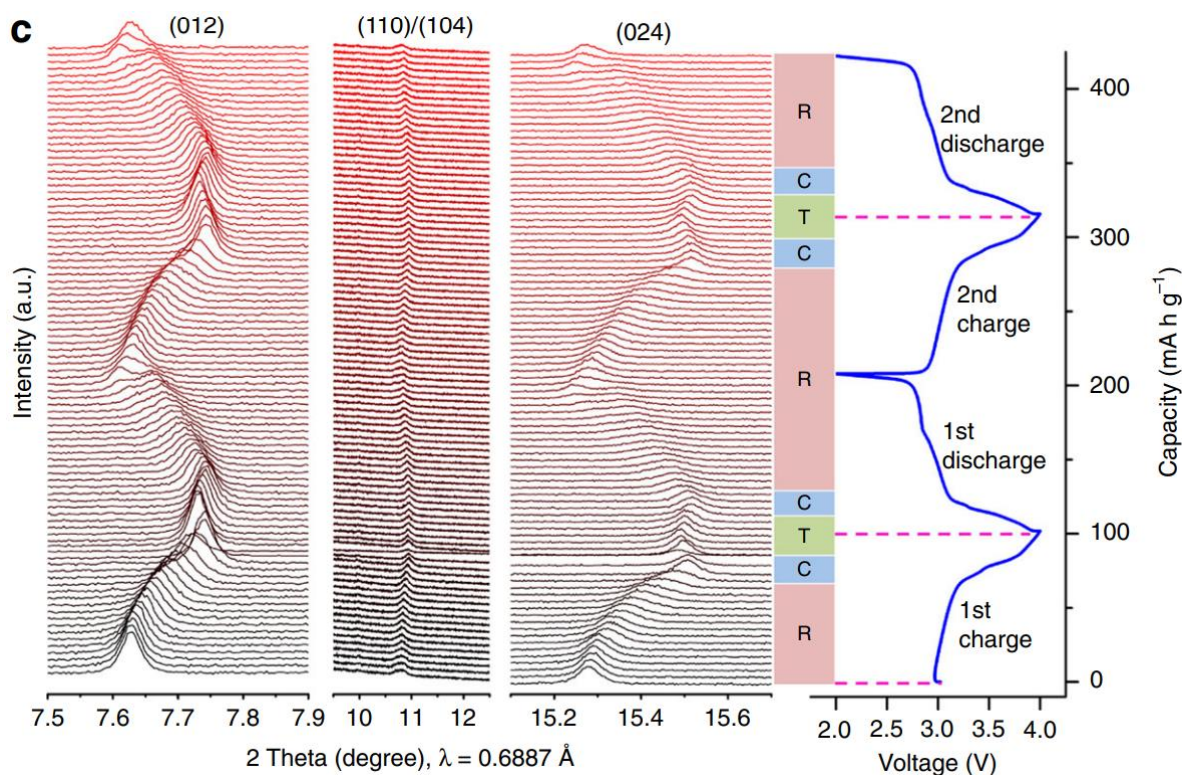


Figure 4

There are more than a thousand words needed to fully describe this data. However, to understand quickly what the Figure means, I think it is best to look at the R, C, and T portions of the graph. Rhombohedral (R) means the cathode is well sodiated (i.e. $0 \leq x \leq 0.4$ roughly) and the cell is lower in charge. As the cell charges, Na⁺ leaves the lattice and gets plated on the sodium metal anode in this case (half-cell). When the sodium content is very low in the material, it will enter the tetragonal phase (T). In the absence of sodium, the responsibility of coordinated water to

stabilize the lattice becomes heavier. Water behavior is difficult to characterize during operation, which is good reason to study the system after it has been dehydrated.

My main criticism of the Gu et. al (2020) paper was that it lacked a conclusion. Some of the conclusions were discussed in the body sections, but after reading the full text, I felt like there was no excitement that I perceived from the abstract. Later, I realized the team published just recently in March 2022 with a strong experimental conclusion that dehydrated $\text{Na}_{1.76}\text{FeFe}(\text{CN})_6 \cdot 2.6\text{H}_2\text{O}$ exhibited improved cycling stability at higher temperatures. From my perspective, this experimental conclusion coincides well with the computed enthalpies of formation from the Ong et. Al paper. Below in right graph of Figure 5, the HSE computations predict a stable monoclinic phase for dry $\sim \text{Na}_{1.1}\text{FeFe}(\text{CN})_6$. This means when the voltage of the battery at $\sim 298\text{ K}$ passes a value corresponding to $\text{Na}_{1.1}\text{FeFe}(\text{CN})_6$, the active material is paying an enthalpic price to carry on operation. If the battery is operating at temperatures like those studied (333 K), this thermal energy could contribute enough Gibbs free energy to counteract some of the enthalpic loss during phase transitions. The left graph in Figure 5, may also support the evidence of higher room-temp energy performance demonstrated by $\text{Na}_{2-x}\text{MnFe}(\text{CN})_6$.

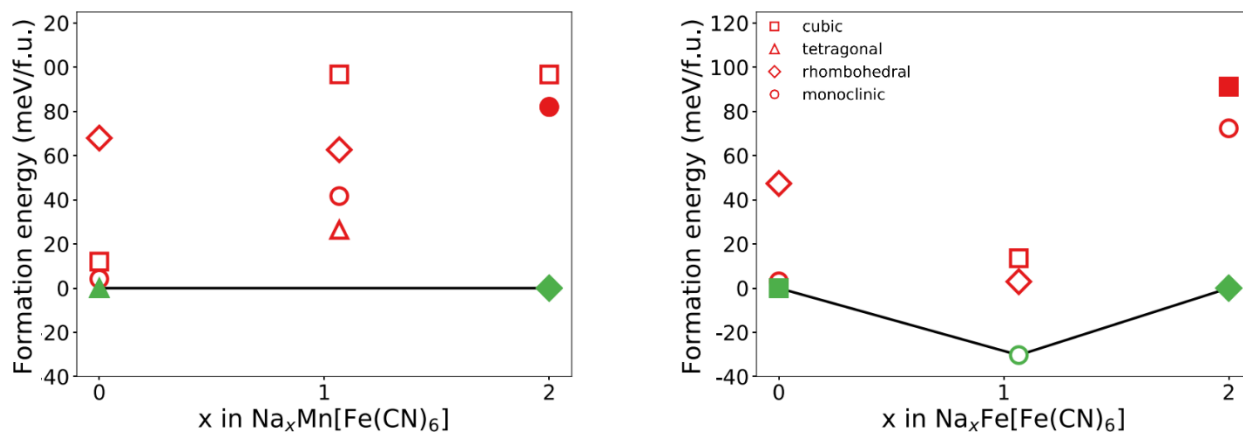


Figure 5

Regarding the paper by Ong et. al, my main criticism was that they never provided any reasoning for why the generalized gradient approximations (PBE, PBEsol, GGA) did not lead to successful values. I think they should have stated their intention for discussing these computational techniques because as a reader I am not sure if they are applying pressure on *Materials Project* database to update their values or if they are suggesting they need to refine their own parameters for future work. There are many things I do not fully understand about the mechanisms discussed in the papers, especially the density-functional-theory (DFT) algorithms. I am also having some trouble verbalizing in my own words how the stability of the tetragonal phase is maintained for dehydrated PBA batteries. I think the reason the phase is stable and does not become reduced is due to the Argon environment during heat treatment process. This is not explicitly stated in the Gu et al. (2022) paper but can be inferred from their conclusion section.

Conclusion

Personally, I haven't been this excited about a specific battery chemistry since I was working on the frustrating silicon anode back in 2016. I see this technology dominating the lower-budget energy storage market because it is already being commercialized and it is miraculously affordable given the application. At an approximate cost \$6 / kWhr and free of conflict metals, the only thing holding this chemistry back from conquering the market is the lack of energy density. Furthermore, it should be noted that despite the presence of cyanide ligands in the material structure, sodium ferrocyanides are of low toxicity as they rarely generate free cyanides⁶. The most hazardous materials in these liquid-electrolyte cells are the organic carbonates and other solvents used to synthesize the electrodes. I would love to put a few of these Natron pouch cells in my closet to help offset the insane price of grid energy in San Diego.

I am very grateful to have had the opportunity to research these materials as a class project because I intend to apply for battery scientist positions at Natron Energy Inc. (Santa Clara) and Tesla (San Diego) in the near future! I will also use this knowledge gained to explore some theoretical approaches to battery modeling. I am always trying to capitalize on my strengths and improve my weaknesses, which for me means continued attention to detail in the laboratory and more practice on relevant software respectively.

References

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