# Report for Cesium Additives for Boosted Stability of Rechargeable Batteries

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## Summary

The aim of the project was to synthesise iron based cesium containing Prussian blue analogues and investigate the effect cesium has on stabilising the Prussian blue structure during synthesis and subsequently during electrochemical cycling with the objective to boost electrochemical performance by preventing a structural phase transition. In order to meet these aims, a series of cesium containing Prussian blue samples were synthesised via a co-precipitation method in an acidic reducing solution. We successfully produced Prussian white with partial substitution of Na for Cs. The composition seems to follow the stoichiometric mixture of Na and Cs in the initial reaction vessel, adding confidence to our observations. Addition of Cs favors cubic symmetry, likely due to the larger size of Cs, as predicted. However, the samples appear to be more sensitive to humidity converting to cubic Prussian blue and $Na_4Fe(CN)_6$, whereas the non-cesiated structure remains largely unchanged. The dehydration properties of the material also changed, with a more gradual removal of moisture compared to the Cs free samples. Upon dehydration, most samples distorted to the rhombohedral structure with the exception of the highest Cs-content sample (x=0.239 in $Na_{2-x}Cs_xFe_2(CN)_6 \cdot yH_2O$) which formed a mix of cubic and rhombohedral structures. Given the huge parameter space in synthesizing Prussian blue combined with the challenges in determining composition further work will need to be performed to confirm our observation that Cs stabilizes the cubic structure and to understand why the samples are sensitized to moisture. With thoroughly characterized samples, electrochemical testing can begin.

## Introduction to the Project

The initial project plan was to be a pilot study into the feasibility of using Cs as an additive in sodium ion batteries with an extended outlook of exploring the feasibility of an all cesium cell utilizing polymer electrolytes. The plan was to incorporate Cs in the electrolyte as an additive and investigate the effect of cesium on the positive electrode material $A_xFe[Fe(CN)_6]$ in half cells and then the influence on electrochemical performance in full cells containing $A_xFe[Fe(CN)_6]$ as the cathode and hard carbon as the anode. The key aspects that will be explored are the affect that cesium has on the crystal structure of iron based PB during electrochemical cycling and whether stabilization of the cubic structure results in improved performance. In addition, Cs can be incorporated into the PB structure during synthesis, rather than being included as an electrolyte additive. Thus, this path to Cs inclusion should also be explored. Finally, once the influence of Cs in a half cell is established, the study will be expanded to testing full cells with hard carbon. In this type of cell, both anode side reactions which consume Cs in the formation of the SEI and Cs insertion into the cathode will be at play. The project thus aimed to address the following questions:

- How does Cs insertion change the structure of AxFe[Fe(CN)6]?

- What concentration of Cs in the electrolyte is necessary to stabilize the cubic structure of $A_xFe[Fe(CN)_6]$?

- Can Cs ions be used as a templating agent to encourage the formation of cubic high sodium content AxFe[Fe(CN)6] during synthesis?

- Does Cs inclusion improve cycle life of PB containing sodium half cells?

- Does the inclusion of hard carbon for the anode consume Cs in the SEI reducing the availability for stabilizing the PB structure?

## Methods and Analysis

**Personnel**

For this project, one postdoctoral researcher, a PhD student and one masters student were utilized to undertake the work. The PhD student performed the initial electrochemical characterization, the postdoctoral researcher contributed towards the synthesis, characterization and data analysis whereas the masters student largely played a role in setting up the synthesis and initial characterization. The bulk of the work has taken place during 2019.

**Synthesis**

The Prussian blue (PB) samples where synthesized using the co-precipitation method in an acidic reducing solution from sodium ferrocyanide and iron (II) chloride, with cesium chloride added to the sodium ferrocyanide solution in different stoichiometric quantities to produce differing cesium content in the final product. Deionized water, concentrated HCl (0.1 M) and ascorbic acid (10 mM) where added to a parent reactor. In addition, two separate aqueous reactant solutions where prepared: $FeCl_2$ (1.28 M), and Na4Fe(CN)$_6$ (0.28 M) and CsCl (0, 8.2, 27, 55 or 120 mM). The reactant solutions where prepared at least 12 h before the experiment was started. All solutions where bubbled with $N_2$ gas and the reaction vessel heated to a nominal temperature of 80 °C in an oil bath

1 h before the reactants were added using peristaltic pumps to the parent reactor. The $FeCl_2$ solution was added at a rate of 0.26 ml * $min^{-1}$ and Na4Fe(CN)$_6$ + CsCl at 1.22 ml * $min^{-1}$ over 4 h. After addition the solutions were allowed to age over 12 h under heating and stirring and was suction filtered and washed three times with heated $N_2$ bubbled deionized water. Finally the precipitate was dried in flowing $N_2$ while heated to 60 °C, except for the highest cesium containing sample which was dried at room temperature under $N_2$ flow after rinsing with $N_2$ bubbled ethanol. Parts of the samples were heated to 200 °C under vacuum and stored in an Ar glovebox.

The graphs and calculations in this paper where produced using the matplotlib[1], pandas[2] and numpy[3] libraries.

**Electrochemical tests**

Galvanostatic cycling was performed in 12mm diameter Swagelok cells. The Prussian White powder was mixed with 25 wt% conductive additive (C-nergy super C65) using a mortar and pestle in argon atmosphere. During assembly 10.1 mg of active material was transferred onto an aluminium current collector in the Swagelok-cell and two layers of glass fibre separator was placed between the powder and the 11 mm metallic sodium anode. The electrolyte consisted of 1.5 M NaPF6 (Stella) in DME. Cs was included as an additive in concentrations of (0.1 M and 0.2 M). Cycling was performed using a LAND CT2001A battery tester between 4 & 2 V vs. sodium.

**Microscopy**

The morphology and composition was studied using a LEO 1530 Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray Spectrometer (EDS). Morphology analysis was carried out on sample applied to carbon tape and EDS on compressed 5 mm disks of the samples.

**Thermal Analysis**

Thermogravimetric analysis (TGA) was carried out by a TGA Q500 instrument under either flowing Ar, $N_2$ (60 ml/min) with the heating rate of 5 °C/min in the temperature range of 25-500 °C. Samples (~10 mg) were mildly ground, left to equilibrate under ambient humidity and placed in alumina crucibles.

**X-ray diffraction**

Samples were characterized in house using a Bruker D8 advanced and a STOE Stadi P using CuKα radiation, and on the P02.1 beamline at the DESY synchrotron using 0.20721 Å radiation. The STOE and DESY samples were prepared in glass capillaries and the D8 samples where applied on a zero-background single-crystal Si disk after dispersion in ethanol.

The structures of the samples where refined using the Rietveld method [4] in FullProf[5]. As Cs and Na share the same position the occupancy of both could not be reliably refined. The Cs occupancy was fixed as the mean of the values obtained from the iron cesium ratio from EDS assuming full iron occupancy and the Na occupancy was allowed to vary freely.

## Summary of Results

**Initial Cs uptake study**

Initially, the aim was to investigate whether Cs uptake into $Na_2Fe[Fe(CN)_6]$ (PW) occurred in an electrochemical cell if it was included as an additive in the electrolyte. However, according to postmortem EDS measurements there was no Cs present in the sample after 10 cycles. This

experiment was followed with testing Cs uptake into PW from a concentrated CsCl solution. However, again, no Cs uptake was observed via this method. Thus, from this point, the project instead focused on synthesizing Cs containing PW from the beginning. Here a series of samples were targeted with increasing Cs content to directly observe the influence of Cs on the structure and properties.

**Synthesis of Cs-containing PW**

The syntheses produced light blue powders comprised of cubic particles with sides in the order 6-100 μm (Figure 1, Left), no obvious difference in the particle size distributions were observed. The amount of Cs in each sample was measured using EDS on a number of separate particles in each sample. Assuming that the iron sites are fully occupied the amount of Cs in the sample, given as x in $Na_{2-x}Cs_xFe_2(CN)_6 \cdot yH_2O$, is found in Table 1 and Figure 1 Right. The values given are estimated using Bayesian inference where $x_{Cs, sample}$ ~ Flat(lower=0, upper=2), σ ~ Exponential(λ=1), and $x_{Cs\ obs}$ ~ Normal(μ= $x_{Cs, sample}$ σ=σ) in pymc3[6] using the NUTS sampler[7].

Comparing the $x_{Cs}$ from EDS to what would be expected for a stochastic or complete preferential uptake of Cs (Table 1 and Figure 1 Right) in the samples it seems that $x_{Cs}$ is slightly larger than stochastic uptake but far from complete absorption of all Cs. The amount of Cs in each the grains of the same sample was close indicating an even uptake of Cs in all particles.

*Table 1 $x_{Cs}$ expected at different concentrations of CsCl if stochastic or complete Cs uptake is assumed and the mean $x_{Cs}$ of the samples with a 95% credibility interval.*

| $c_{CsCl}$/mM | $x_{Cs}$ stochastic | $x_{Cs}$ complete | $x_{Cs}$ (50%, [2.5%, 97.5%]) (EDS) |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 8.2 | 0.015 | 0,059 | 0.017 [0.014, 0.020] |
| 27 | 0.047 | 0,19 | 0.046 [0.042, 0.049] |
| 55 | 0.094 | 0,39 | 0.109 [0.106, 0.112] |
| 120 | 0.194 | 0,86 | 0.239 [0.235, 0.242] |



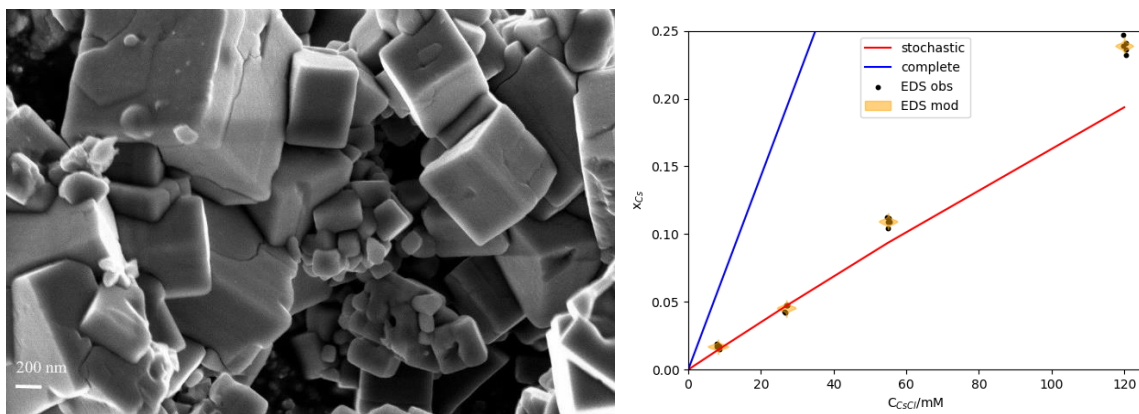*Figure 1, Left:* SEM image of $x_{Cs}$=0.017. Right: EDS results of Cs content in Cs substituted PW produced from solutions with varying Cs content. The blue line indicates the content if 100% uptake is assumed.

As synthesized samples were monoclinic ($x_{Cs}$=0%, 1.7% ), a mixture between monoclinic and cubic (4.6%, 10.9%) or cubic (23.9%).

**Behaviour of Cesiated PW**

Typically when preparing PW samples prior to incorporation in an electrochemical cell the sample is dried to remove water from the structure. For the sodium rich PW phases this dehydration occurs over a narrow temperature range between 170-220°C. Contrary to this, the cesiated samples exhibit a gradual release of water over a temperature range that widens for higher cesium contents (Figure 2, Table 2).

*Table 2 Proportion of water released over two different temperature ranges. The total water content released remains approximately the same.*

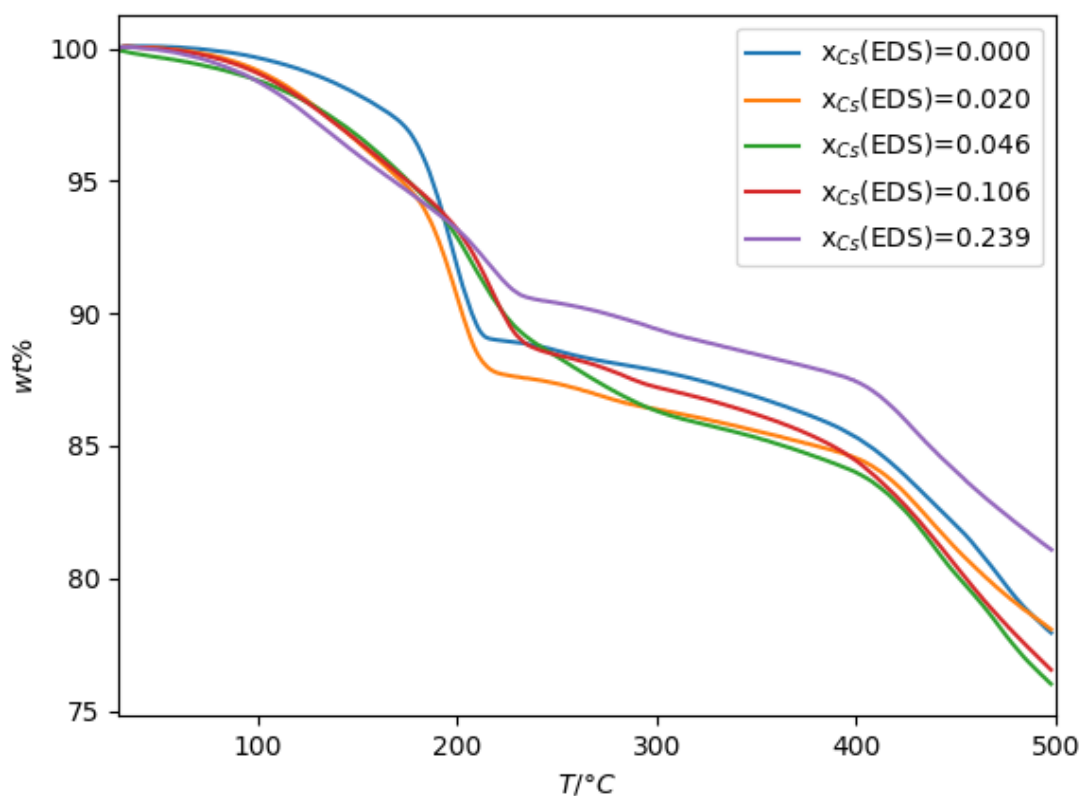| $x_{Cs}$ (EDS) | Uncoordinated or surface water (30- 175 °C) | Coordinated water (ca 195-220 °C) |
|---|---|---|
| 0 | 0.49 | 1.20 |
| 0.017 | 0.91 | 0.99 |
| 0.046 | 1.00 | 0.69 |
| 0.109 | 0.96 | 0.67 |
| 0.239 | 1.31 | 0.39 |



*Figure 2: TGA curves for PW containing different proportions of Cs, recorded in flowing N2 at a heating rate of 5 °C min$^{-1}$*

In addition to a change in the nature of water removal the change of structure following the release of water is also different in the cesiated compounds. Heat treatment at 200 °C for 20 hours turned the samples orthorhombic (0%, 1.7%) or mostly orthorhombic ($x_{Cs}$=4.6%, 10.9% and 23.9%). Further, after storage in ambient conditions for 4 months all as synthesized (non-dried) samples containing Cs converted to a mixture of cubic phase and what is predicted to be $Na_4Fe(CN)_6$ based on matches to peaks observed from a dehydrated $Na_4Fe(CN)_6.10H_2O$ sample (Figure 3).
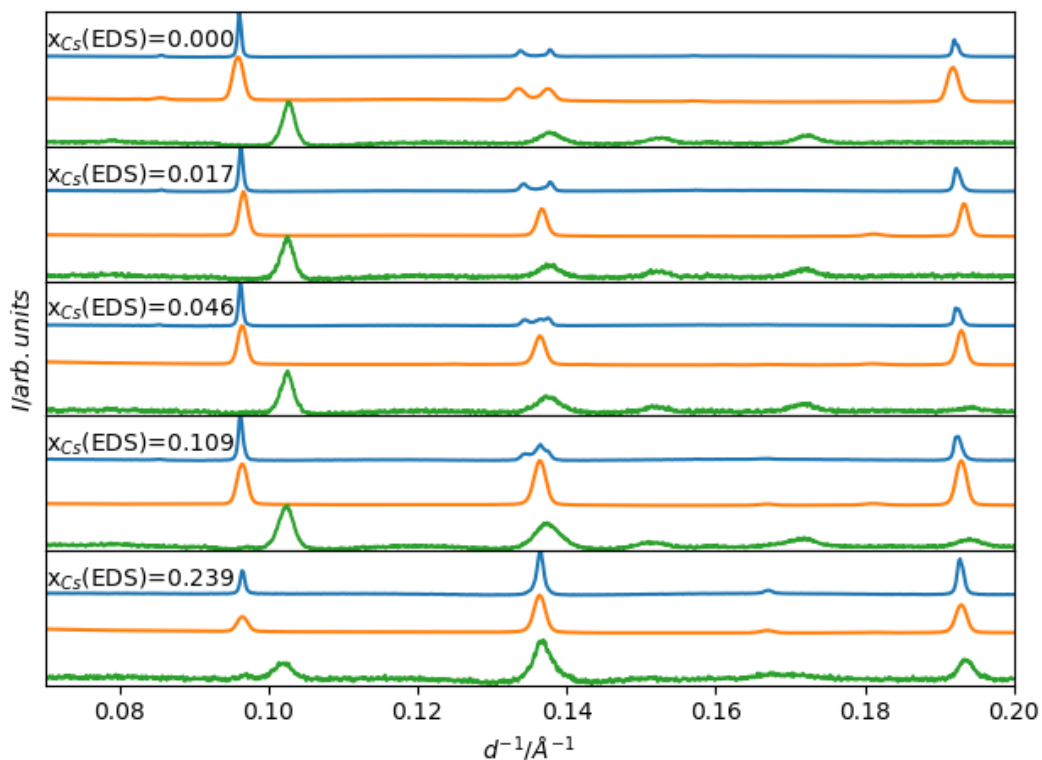
*Figure 3: Powder x-ray diffractogram of samples as synthesized (blue), after storage (orange) and heat treatment at 200 °C during 12 h (green). The diffractograms are measured on the D8, STOE and P02.1 beamline at DESY respectively, so no conclusions should be drawn from the peak widths or signal to noise levels.*

From the above results it seems that Cs stabilizes the cubic structure. Firstly samples with Cs content above 6% are partly or fully cubic as synthesized and secondly conversion to rhombohedral is less complete after 20 h at 200 °C under vacuum. Finally, all samples with any Cs content decomposed to cubic phase or where still cubic after 4 months storage at ambient conditions.

## Conclusion

Initial measurements have demonstrated that we have successfully synthesized Prussian white with partial substitution of Na for Cs. The structure of the prepared samples behaves in a way that is in line with predictions that the presence of Cs can stabilize the cubic structure and potentially reduce the presence of strain. The upper limit of Cs inclusion and the point of complete stabilization of the cubic structure still must be explored. While complete cesiation was not observed according to the amount of Cs in the reaction mixture, the composition seems to follow the stoichiometric mixture of Na and Cs in the sample. While this is the case, many of the analysis methods were performed with the assumption that there were no Fe vacancies. This will need to be measured and the Cs content determined via a method with a higher accuracy than EDX (for example, Rutherford backscattering as Inductively coupled plasma optical emission spectroscopy cannot measure Cs). Precisely characterizing the material is essential to actually understanding why it behaves the way it does. This is even more vital for electrochemical testing where even more variables are introduced. Thus, after this initial study the following questions remain: Why does the dehydtration behavior change and does the gradual release of water reduce strain? Does the tendency towards cubic structures extend to electrochemical cycling? A separate follow up project dedicated to exploring the effect on electrochemical cycling and influence on SEI formation will also need to be performed.

# References

1. Hunter, J.D., *Matplotlib: A 2D Graphics Environment.* Computing in Science & Engineering, 2007. **9**(3): p. 90-95.
2. McKinney, W., *Data Structures for Statistical Computing in Python.* Proceedings of the 9th Python in Science Conference, 2010: p. 51 - 56.
3. Walt, S.v.d., S.C. Colbert, and G. Varoquaux, *The NumPy Array: A Structure for Efficient Numerical Computation.* Computing in Science & Engineering, 2011. **13**(2): p. 22-30.
4. Rietveld, H., *Line profiles of neutron powder-diffraction peaks for structure refinement.* Acta Crystallographica, 1967. **22**(1): p. 151-152.
5. Rodriguez-Carvajal, J., *Fullprof: A Program for Rietveld Refinement and Pattern Matching Analysis.* Abstract of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, 1990: p. 127.
6. Salvatier, J., T.V. Wiecki, and C. Fonnesbeck, *Probabilistic programming in Python using PyMC3.* PeerJ Computer Science, 2016. **2**: p. e55.
7. Hoffman, M.D. and A. Gelman, *The No-U-Turn sampler: adaptively setting path lengths in Hamiltonian Monte Carlo.* Journal of Machine Learning Research, 2014. **15**(1): p. 1593-1623.