POSITIVE ELECTRODE MATERIALS FOR NA AND K ION BATTERIES

Investigating synthesis methods for Prussian Blue and Prussian White

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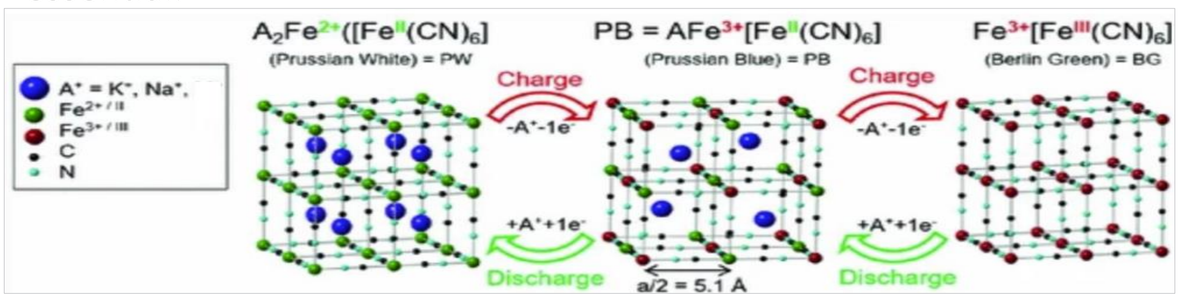
ABSTRACT

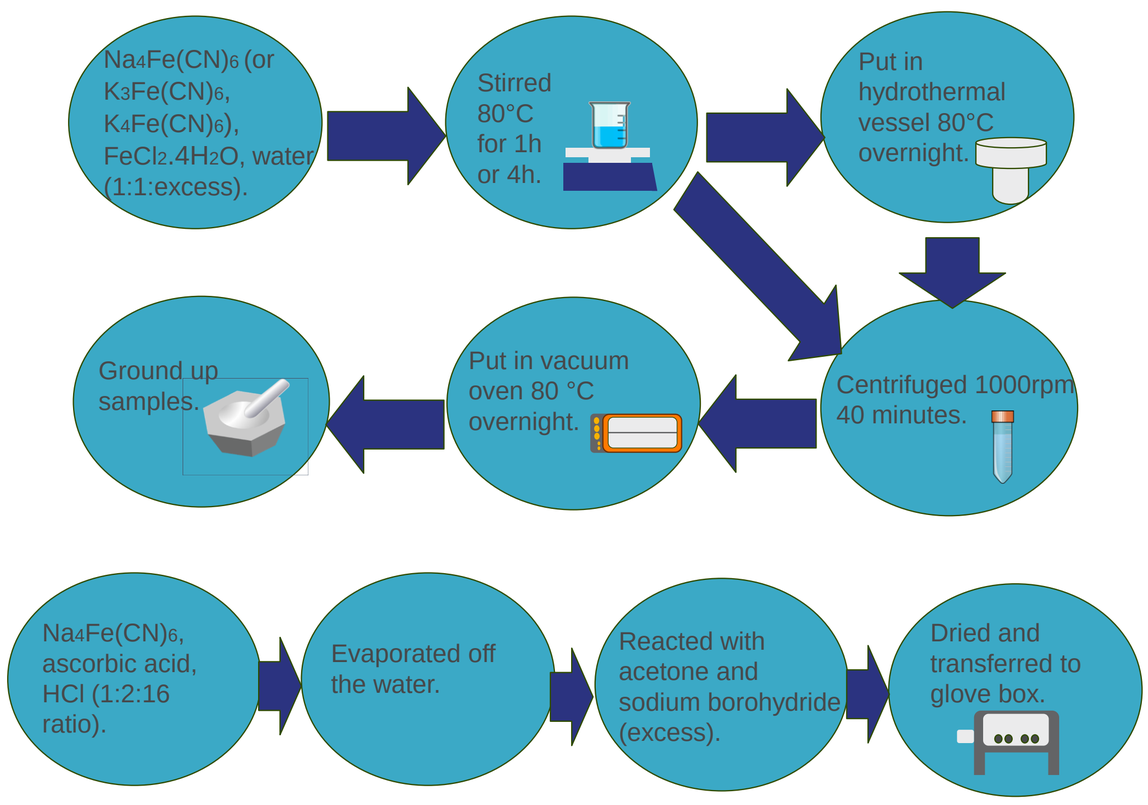
Na and K ion batteries are necessary for the development of renewable energy and storage. Na and K are more abundant than Li and can have a more sustainable supply. Developing electrodes which are as efficient as Li batteries is essential.

MOTIVATION

Prussian Blue (PB) and Prussian White (PW) potentially could be used as a high capacity, long cycle life positive electrode in Na or K ion batteries. Having a reliable synthesis method is essential for the development of these materials.

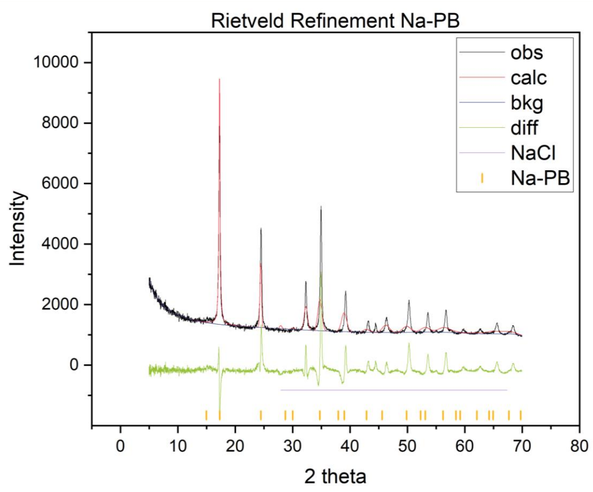


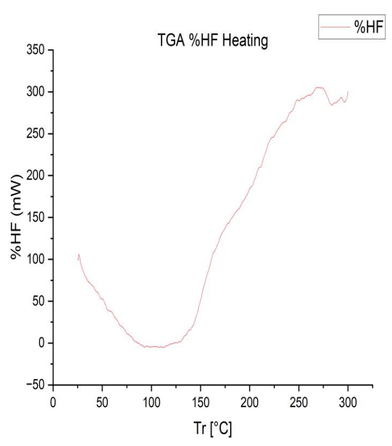
METHODS

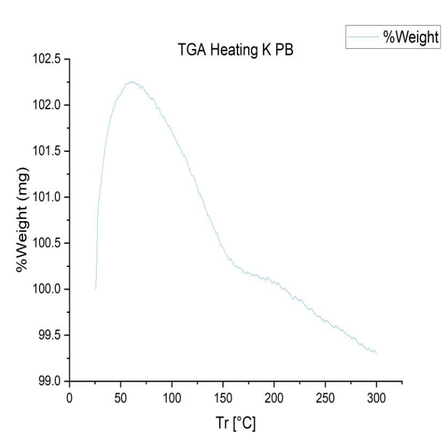


X-RAY DIFFRACTION AND TGA DATA

- Na-PB and K-PB were synthesised.
- Samples contained NaCl and Fe_2O_3, or KCl impurity. KCl almost negligible quantity.
- Using HCl and ascorbic acid starting reagents had lower intensity for the impurities.



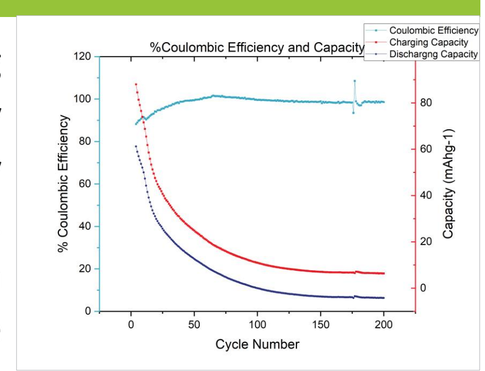


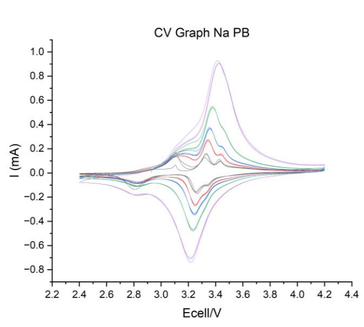


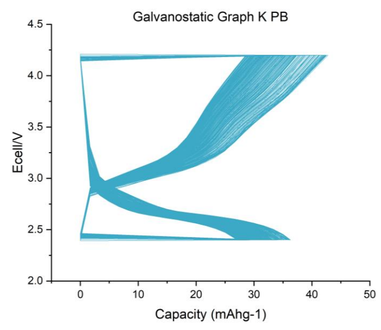
The TGA data shows a weight fluctuation of 3%, indicating a stable phase with only a small loss of water.

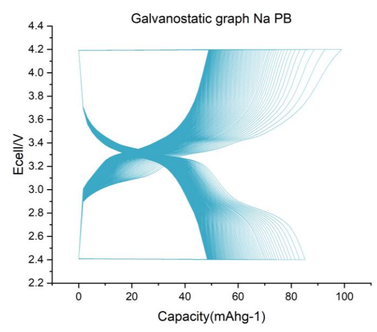
CYCLING AND SEM DATA

Na-PB has a max capacity of 93mAh/g and gradually decreases in capacity before settling at 50mAh/g. K-PB only has a max capacity of 37mAh/g. Primarily this is due to the delamination of the electrodes. The materials are phase stable.

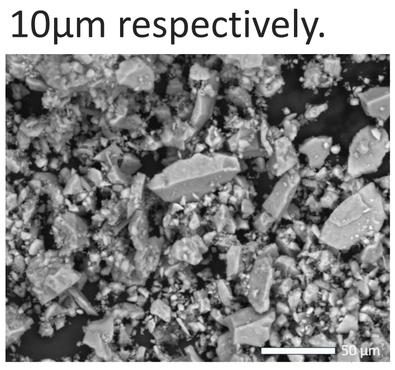


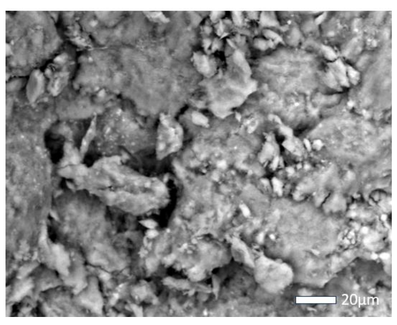


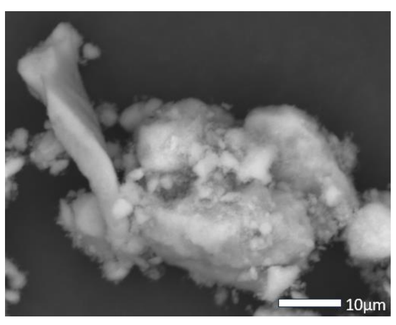




The SEM for K-PB shows 1-2% Cl impurity in the samples. The particle size is small (5µm - 20µm) indicating the formation of nanoparticles. The diagrams below show K-PB at 50µm, 20µm and 10µm respectively.

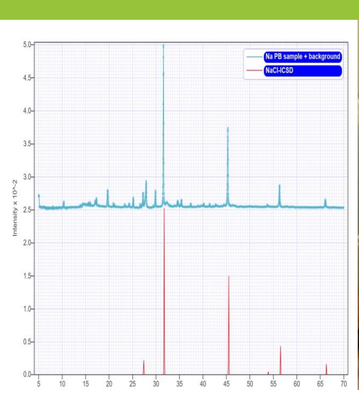






PRUSSIAN WHITE

PW is air sensitive and oxidised back to PB when left in air. Synthesis under $N_{2(g)}$ was more successful, but there was a large NaCl impurity. K-PB did not react with the reducing reagent.



NEXT STEPS

- Repeat the electrochemical tests for the K-PB.
- Investigate more methods for PW synthesis and perform electrochemical tests on it.

CONCLUSIONS

- Co – precipitation method works best with $FeCl_2.4H_2O$ and H_2O, which are therefore better starting reagents than HCl and ascorbic acid.
- Co – precipitation method does require repeated washing.
- Synthesis under 8mmol gives a poor yield.
- $K_4Fe(CN)_6$ is a better starting reagent than $K_3Fe(CN)_6$ for K PB synthesis.
- PW is air sensitive and can only be synthesised using Na PB as the starting reagent in an inert atmosphere.

REFERENCES

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2. W. Brant, R. Mogensen, S. Colbin, D. Ojwang, S. Schmid, L. Häggström, T. Ericsson, A. Jaworski, A. Pell, and R. Younesi, *Chem. Mater. 2019, **31**, 7203−7211*

Intern Bio

Ailsa O'Riordan is a 2nd year Chemistry undergraduate at the University of Oxford. She is interested in batteries and renewable energy and how this can lead to more sustainable energy storage. She is aspiring to do a PhD.

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