FROM GROUND WASTE TO BATTERIES:

Using Prussian Blue from remediated ground waste as cathode material for sodium-ion batteries

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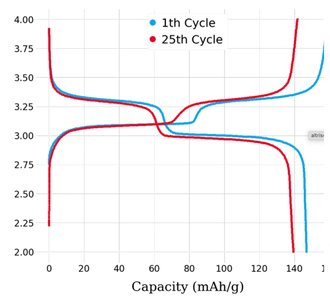
Abstract

- Sodium is globally available and a preferred choice for grid-scale energy storage system. Prussian Blue Analogues (PBAs) are promising cathode materials for SIBs with a practical capacity of 170 mAh/g and relatively high working potential (3.2V vs Na^+/Na)[1] because of their rigid open framework with large interstitial sites[2].
- Blue billy ground waste (GW) has been recognised as a problem effluent and land contaminant since the early industrial period. The extracted Prussian blue from GW can only achieve 48 mAh/g for SIBs, which is due to the low percentage of active material in GW powder.
- Sodiated Prussian blue（PB） with the formulae Na2Fe[Fe(CN)6] is prepared using a simple method reported by Tan et al and made into a slurry under ambient air conditions. Synthesized PB under ambient air can achieve 110 mAh/g for SIBs but decays much faster than PB prepared under vacuum conditions.
- We compare electrochemical performance using galvanostatic tests and structure of extracted PB from Ground waste and synthesized PB via X-ray diffraction methods.

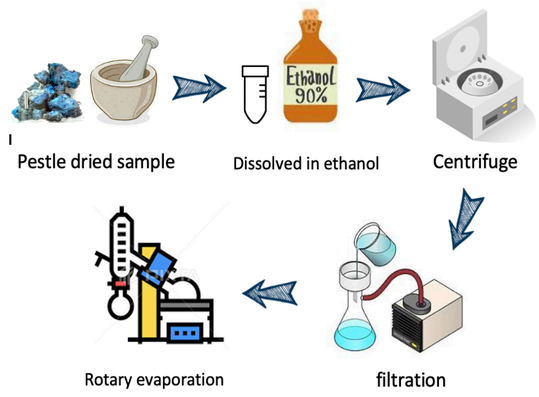
Motivation

- For PB GW project: As one of a range of ferric ferrocyanide, blue billy is a compound mostly of iron, carbon and nitrogen. It may contain Prussian Blue as well as some other impurities. The idea of purifying GW and extracting PB is therefore generated.
- For PB synthesis project: Fennac， also called Prussian white or sodiated PB, is a promising cathode material for commercial SIBs developed by company Altris. Curiosity drives me to dig deeper into how this material can be made.



Methods

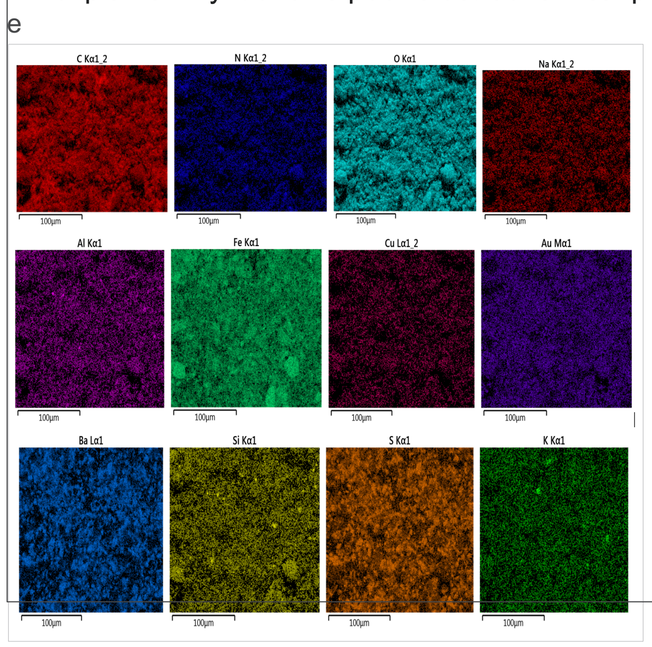
- Extracting Prussian blue from ground waste as followed. PB/super P/ PVDF=7:2:1 mass ratio
- Detailed synthesized PB process can be seen in the paper reported by Tan et al.[3]. The only difference made is slurry is made under ambient conditions instead of vacuum conditions .
- Purification process is as followed.



Characteristics

- Compared with our XRD results (figure f) with literature XRD results (figure g[1]), it shows that shows that synthesized Prussian white is not fully sodiated, it turns back to Prussian blue once it is exposed to air for a long time.
- Except for PB, PB extracted from GW still contains plenty of impurities, constituting interstitial sites probably. EDS(figure e)
- further proves the presence of other elements such as Al Fe Cu Au Ba etc. .That explains why it shows poor electrochemical performance.

e



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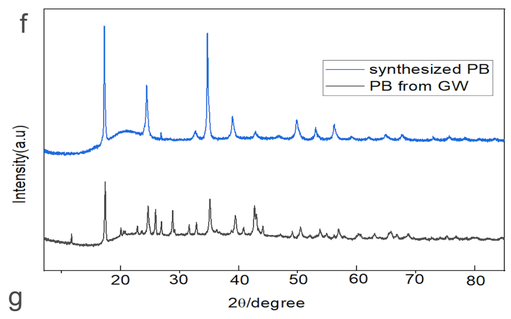

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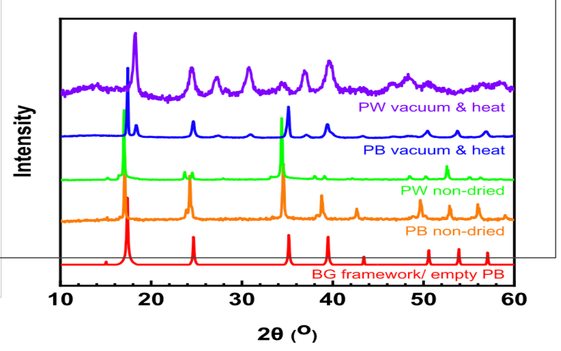
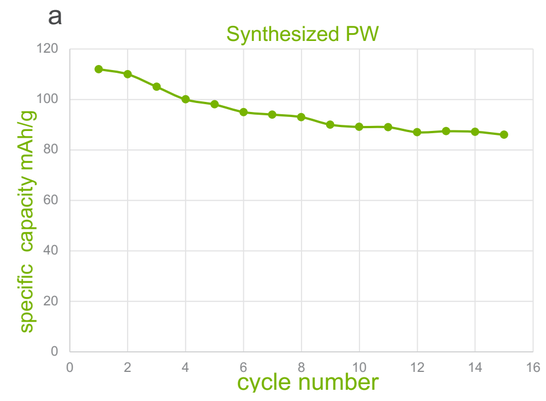


ELECTROCHEMICAL PERFORMANCE

- Figure a,b shows electrochemical performance of synthesized PW. Its maximal capacity is 112 mAh/g and the specific capacity gradually decays to 80mAh/g after 15 cycles. Current used here is 0.1 C and voltage used is 3.8-2 V .
- Figure c,d shows electrochemical performance of GWPB can only reach 48mAh/g, and it decays very fast to 30mAh/g after 15 cycles.

a



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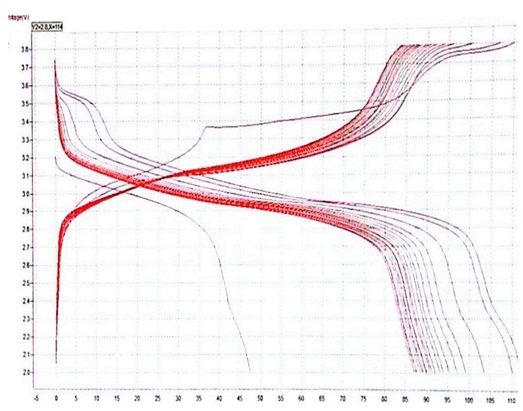

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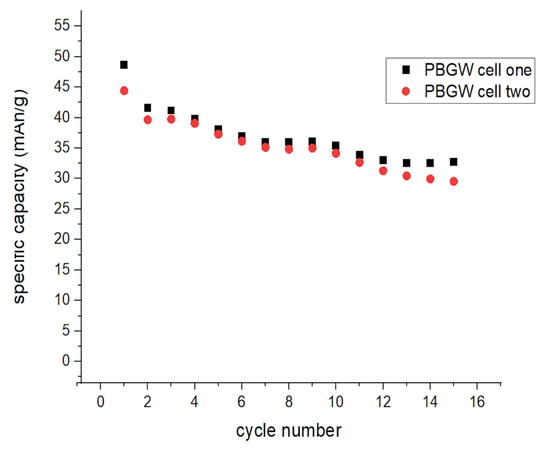

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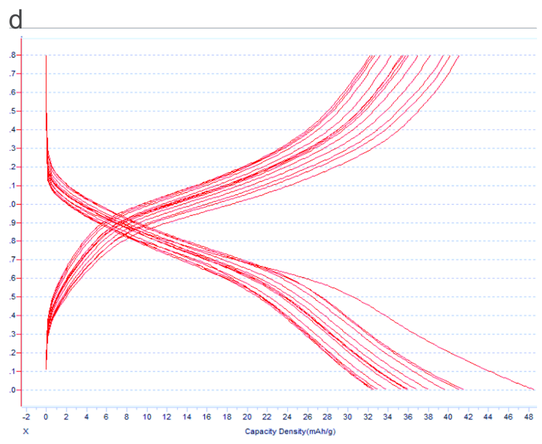

Conclusion

PB from GW cannot be purified by simply being washed with ethanol, leading to poor electrochemical performance. It proves that the facile approach toward the preparation of PW requires strict vacuum condition which is not easily achieved. Exposure to air for a long time reduces capacity of sodiated PB and makes it decay much faster, although partially sodiated PB can still reach about 112 mAh/g at maximal.

Impact / Next steps

- Chemical engineers could work out better ways to purify ‘Blue Billy’ without damaging PB structures.
- During synthesis of sodiated PB, the formation of Ascorbic-PB highly depends on PH value, temperature rise rate and stirring rate. We could research on it later.
- Once PW is exposed to air, PW would easily become slightly blue, which reduces capacity of the cathode material. Procedure should be improved.

References

- 1. J. Qian, C. Wu, Y. Cao, Z. Ma, Y. Huang, X. Ai, H. Yang, *Adv. Energy Mater.* **2018**, *8*, DOI 10.1002/aenm.201702619.
- 2. Karyakin, A.A., *Prussian blue and its analogues: electrochemistry and analytical applications.* Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis, 2001. **13**(10): p. 813-819.
- 3. ACS Appl. Energy Mater. 2021, 4, 6214−6220

Intern bio

Hengyi Zhang. Studying chemistry at Oxford University (Somerville college). Interested in cathode materials of SIBs and LIBs.

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