Optimization of Prussian Blue Analogues for Na-ion Desalination Batteries

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Introduction

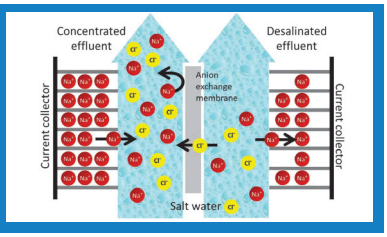
With a growing need for clean water, **interest in capacitive deionization (CDI) is growing** as a potentially low energy methodology.

Commercial technologies use activated charcoal at both electrodes, but these materials suffer from **low capacity and poor durability**.

Inspired by the recent advances in sodium-ion batteries, several studies proposed to use **intercalation materials to increase the desalination potential of electrodes**.

Among the proposed materials for desalination batteries, **hexacyanoferrate Prussian blue analogue materials (PBAs)** are especially interesting because of their open framework structure that allow insertion of Na ions with high reversibility and rapid kinetics.

This study is focused on the development of $NaM_xN_y(HCF)$ PBAs with M and N being Ni, Mn or Fe, with an optimization for performance and durability in 1M NaCl electrolyte.



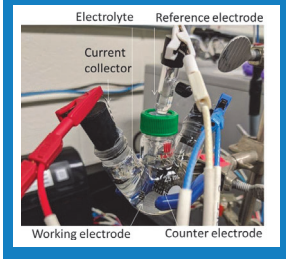
Design of experiment

Synthesis

PBAs coprecipitation synthesis was adapted from ACS Energy Lett. 2020, 5, 100–108 :

- XCl_2 (X = Ni, Fe, Mn) salts were dissolved with $Na_3C_6H_5O_7.2H_2O$ in H_2O in H_2O.
- The salt solutions were then mixed according to target (Mn,Fe,Ni) composition. Nine compositions were tested ().
- 50 ml of the salt solution was then added drop by drop in a solution of $Na_4Fe(CN)_6 \bullet 10H_2O$ under stirring at room temperature.
- Fast stirring was maintained for 24h at room temperature then stopped for 24h.
- Precipitate was then filtered and dried at 120°C under vacuum overnight.

For comparison, a commercial battery graded Fe based PBA was purchased from ALTRIS AB

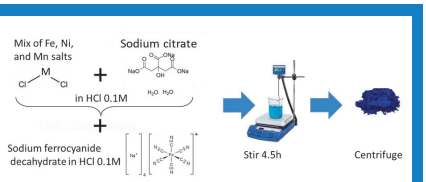


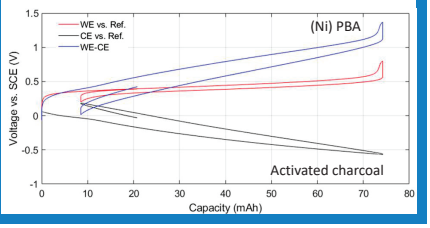
Electrochemistry

Since the aim of the study is to assess the potential of these materials for desalination purposes, only static testing versus a counter electrode was performed.
Electrodes were prepared by mixing the active material with 10% Carbon Super P and 10% PTFE unless specified.
The mixture was then pressed on a titanium mesh. Counter electrodes use activated charcoal.

Electrochemical testing was conduced in 3-neck 50ml flasks with a 1M NaCl electrolyte without any N_2 bubbling to mimic the chemical composition of seawater as close as possible.
Potentials were recorded versus a calomel or a silver/silver chloride reference electrode.

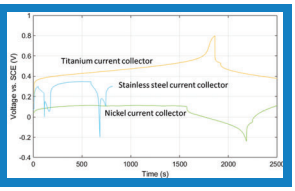
Materials were tested at high rate (up to 64C) to investigate high daily salt adsorption. Results will be reported in mAh/g but also with Salt Adsorption Capability (SAC in mg/g, $Q*3.6/F*M_{NaCl}$) and Average Salt Adsorption Capability (ASAR in mg/g/min).



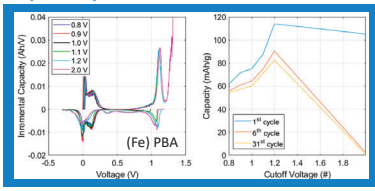


Impact of current collector

Salted water **is highly corrosive.**
Traditional stainless-steel current collectors cannot be used although they work in electrolytes such as 1M Na_2SO_4.
Titanium can be used in salted water without having to remove the oxygen from the water via gas bubbling prior to testing.

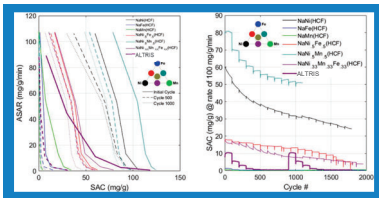


Impact of potential window



PBAs have theoretical capacities in the 110 to 115mAh/g range.
However, these capacities were measured in organic electrolytes with a much larger voltage window.
The additional capacity can be reached by increasing the potential window but parasitic reactions degrades the cyclability.

Performance



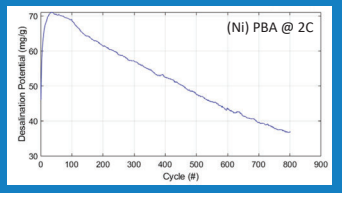
PBA composition has a big impact on performance (capacity, rate capability, and durability).

Best results obtained for the Ni,Mn) PBA, followed by the Ni one.

Measured capacities are, at most, in the 60-70 mAh/g range. This is < $Q_{theoritical}$ (>100 mAh/g) but in line with literature for aqueous electrolytes.

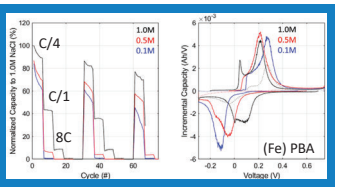
When compared to a commercial PBA our materials performed better, especially at high rates.

With the success of the tests in 1M NaCl with titanium current collectors, some durability testing was undertaken in **real seawater** with a Ni based PBA. The seawater was provided by the University of Hawaii Oceanography department. It was harvested in Station Aloha, a 6-mile radius circle in the Pacific Ocean north of Hawaii. To avoid fouling issues, the seawater was provided to us filtered with a 0.45 micron membrane. The capacity started around 45 mg/g then increased to above 70 mg/g in the first 25 cycles. The origin of that increase is likely induced by improvement in the wettability of the electrodes.



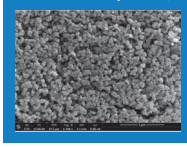
Impact of Electrolyte Concentration

To the contrary of traditional batteries, the **electrolyte composition will change** throughout the charge and discharge cycle **for a desalination battery.**
Lowering the electrolyte concentration is drastically **hampering the capacity retention** because of the **resistance increase**.
A potential solution is to have the electrodes closer together

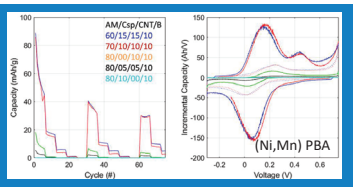


Importance of Synthesis / Storage conditions

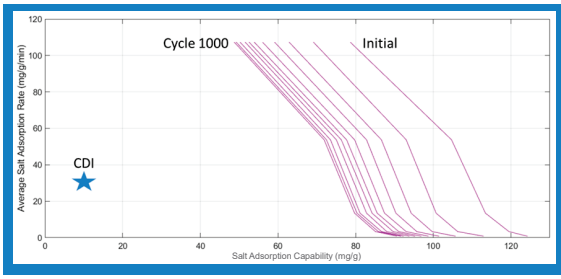
The PBA materials prepared for this study appeared to **be extremely sensible to the synthesis, cleaning, drying, and storage conditions**.



In some cases, performance was suppressed after proper cleaning.
We believe this related to the lack of porosity of pressed electrodes and the PBA morphology. Adding more additives, and in particular CNT, solved the problem and even increased capacity retention.



Conclusions & Outlook



Prussian Blue Analogues **are promising candidates for desalination batteries with good capacity, rate capability, and performance.**

This preliminary work investigated different compositions of PBAs based on Fe, Ni, and Mn synthesized from a coprecipitation method. (Mn,Ni) PBAs offered the best performance with **SAC above 120 mg/g at low rate and above 80 mg/g at rates above 100 mg/g/min**. This is far above classic CDI material performance at around 10 mg/g at a rate of 30 mg/g/min. **After 1,000 cycles, our material still maintained a SAC around 50 mg/g at rates above 100 mg/g/min**.

Further work is in progress to **optimize the electrode further** and improve performance and durability.
There seems to be a high impact of the **synthesis, washing, drying, storage condition, and electrode architecture on performance**. The synthesis and the electrode preparation must therefore be very well controlled.
Moreover, **more work is needed to transfer the excellent performance observed in 1M NaCl to electrolytes with salt concentration below 0.5M** in order to be applicable for desalination batteries.

Acknowledgments

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Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect those of the sponsor.

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