Electrochemical Behavior of Prussian Blue Analogues $Na_xMn[Fe(CN)_6]$ using *water-in-salt* Electrolyte for Sodium-Ion aqueous batteries

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RESUMO

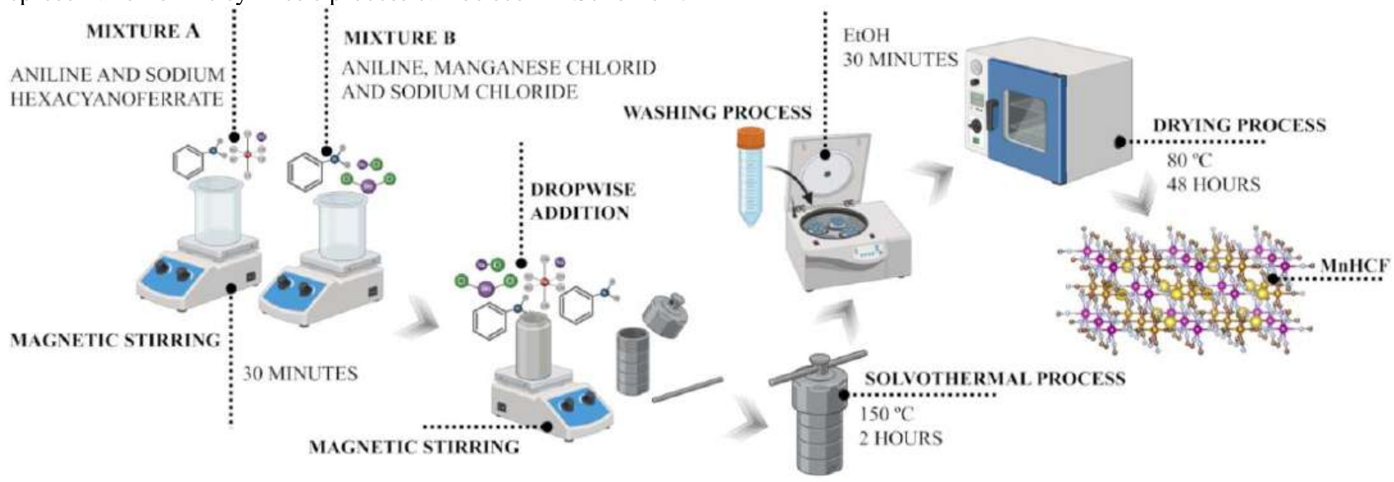
Sodium-ion batteries are promising energy storage systems and a viable alternative to lithium-ion batteries, owing to sodium's abundance and low cost. However, the use of aqueous electrolytes remains limited by the narrow electrochemical stability window (ESW) of water. In this context, *water-in-salt* electrolytes (WiSEs) offer a strategy to widen the ESW and enhance performance. Among suitable cathode materials, Prussian Blue analogues (PBAs) are attractive due to their low cost, ease of synthesis, and high-power density. In this work, a PBA-type $Na_xMn[Fe(CN)_6]$ was synthesized via a solvothermal method (150 °C, 2 h) and applied as electrode material for Na-ion aqueous batteries using WiSEs. The material exhibited clear redox activity and delivered a specific capacity of 479.16 C g^{-1} at C/5. These findings indicate that MnHCF is a promising and low-cost candidate for sodium-based aqueous energy storage systems using WiSEs.
Keywords: Prussian blue, solvothermal synthesis, battery, supercapacitors.

Introduction

Electrolytes play a key role in the performance and safety of electrochemical energy storage devices. Although organic electrolytes are efficient, they are flammable, involve costly manufacturing processes, and pose significant operational risks. In contrast, aqueous electrolytes emerge as a safer and more cost-effective alternative. However, their application is limited by the narrow electrochemical stability window (ESW) of water and issues related to electrode corrosion (1). In this context, *water-in-salt* electrolytes (WiSEs) have attracted attention as a promising strategy to address these limitations. By significantly reducing water activity and promoting the formation of a stable solid-electrolyte interface (SEI), WiSEs expand the ESW and suppress the dissolution of electrode materials. Additionally, the altered solvation structure in WiSEs minimizes the presence of free water molecules, thereby stabilizing the SEI and reducing the reactivity of water in the system (1,2). From this perspective, aqueous sodium-ion batteries (SIBs) are positioned as strategic alternatives to lithium-based batteries, due to the abundance and low cost of sodium. Among the cathode materials compatible with Na^+ insertion, Prussian Blue analogues (PBAs) stand out for their easy synthesis, low cost, and high power density (3,4). In this work, a Prussian Blue analogous – $Na_xMn[Fe(CN)_6]$ (MnHCF) – was synthesized via a solvothermal route, characterized by X-ray diffractometry (XRD), and evaluated as an active electrode material for Na^+-ion aqueous battery using WiSEs.

Experimental part

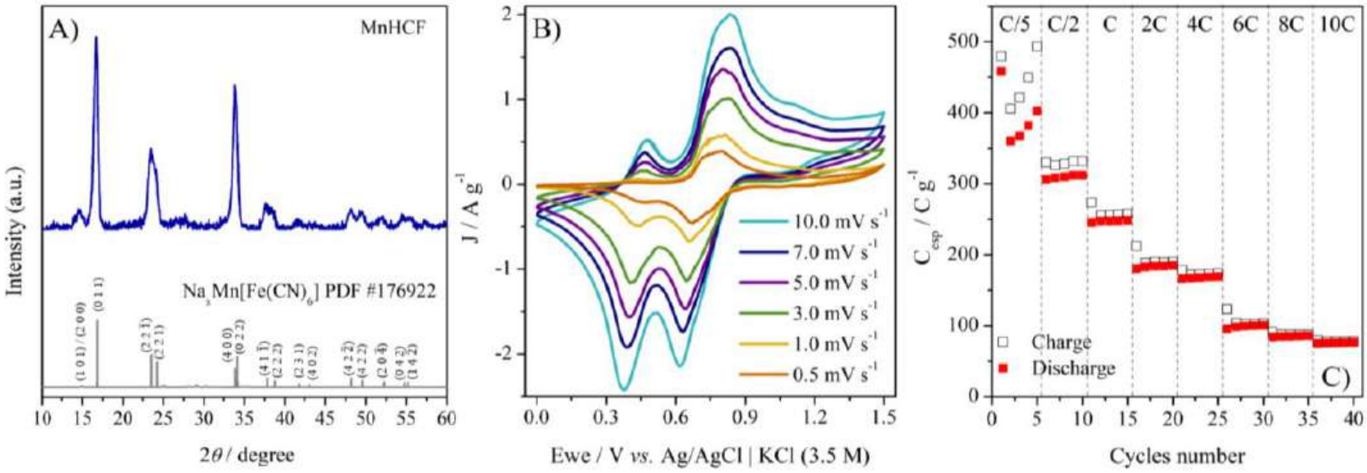
The MnHCF synthesis procedure initially involves the preparation of two distinct solutions, mixture A and B, composed of aniline and sodium hexacyanoferrate, and aniline, $MnCl_2$, and NaCl, respectively, both under magnetic stirring for 30 minutes. Mixture A is then added dropwise to Mixture B, remaining under magnetic stirring, and then autoclaved and heated at 150 °C for 2 hours. The resulting product is washed and oven-dried at 80 °C for 48 hours, resulting in the final MnHCF material. A schematic representation of the synthesis process can be seen in **Scheme 1**.



Scheme 1. Schematic representation of the synthesis process of MnHCF.

Results and Discussion

The X-ray diffraction (XRD) pattern (**Figure 1A**) confirms the successful synthesis of MnHCF (manganese hexacyanoferrate), which adopts the monoclinic structure (*$P2_1/n$*) typical of PBAs, with characteristic reflections matching the reference pattern for $Na_xMn[Fe(CN)_6]$ (PDF #176922). The sharp and intense peaks indicate good crystallinity with no detectable impurities. Crystallite size was calculated using the Scherrer equation, revealing to be 15.05 nm. The electrochemical performance of MnHCF was evaluated in conventional cell, composed of three electrodes immersed in an electrolyte, employing a fiberglass membrane as a separator between the working and the counter electrodes. Electrochemical tests were carried out using cyclic voltammetry (CV) and galvanostatic charge and discharge (GCD) techniques, with a 17 molal $NaClO_4$ *water-in-salt* electrolyte. **Figure 1B** shows the CV curves recorded at scan rates ranging from 0.5 at 10 mV s^{-1}. The material exhibits reversible redox processes attributed to $Mn^{2+/3+}$ and $Fe^{2+/3+}$ couples, maintaining stable performance across various scan rates. **Figure 1C** summarizes the specific capacity values (C g^{-1}) as a function of the number of cycles, corresponding to C-rates from C/5 to 10C. At the lowest rate (C/5), MnHCF exhibited a high specific capacity of approximately 458.39 C g^{-1}. As the current rate increased, a gradual decline in specific capacity was observed — reaching 77.80 C g^{-1} at 10C. Despite this capacity fade, the electrode retained a significant portion of its performance, demonstrating good rate capability and fast charge/discharge response. The narrow gap between charge and discharge capacities at each rate (except at C/5) reflects high coulombic efficiency. Furthermore, capacity values remained stable throughout cycles at each C-rate, highlighting the structural integrity and reversibility of the redox processes. These results confirm MnHCF as a promising material for high-performance energy storage applications requiring rapid charge/discharge rates.



Conclusions

The results demonstrate that the synthesized MnHCF material exhibits a well-defined crystalline structure with no detectable impurities. The material displays reversible redox activity and favorable kinetic for Na^+ ions insertion and extraction. Furthermore, the study at different C-rates shows that the material delivers significant specific capacities at both and low (479.16 C g^{-1} at C/5) and high (77.80 C g^{-1} at 10C) charge/discharge rates, highlighting its potential as a promising candidate for electrochemical energy storage devices operating in aqueous electrolytes, particularly *water-in-salt* systems.

References

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