

Synthesis and Characterization of Prussian Blue Analogues as Cathodes for Sodium-ion Batteries

Leonardo SBRASCINI – *University of Camerino*

Owing to the natural abundance of Na on Earth's crust and its similar chemical reactivity as compared to Li, Sodium-ion batteries (SIBs) have rapidly emerged as a suitable alternative to existing Li-ion batteries [1]. Nevertheless, the development of low-cost cathode materials is still a critical point for these systems. Among the cathode materials, Prussian blue and its analogues (PBAs) are regarded as some of the most promising compounds, thanks to their open framework for fast ion diffusion, possibility to tune their composition and low cost of the constituent elements [2]. However, according to the synthetic approach and the sodium content, these compounds can exhibit a number of different structures, often with a high amount of defects if interstitial water is incorporated, due to the substitution of Fe[CN]6 groups [3]. In this work, we propose a simple room temperature synthesis of a mixed Fe,Mn PBA by coprecipitation under inert atmosphere. The synergistic effect of acetylsalicylic acid as a complexing agent for Mn²⁺ ions, and sodium ascorbate as both a complexing agent and antioxidant molecule [4,5], is evaluated during the synthesis to slow down the formation of the compound and provide a material with a high Na content and a low number of structural defects. The synthesized material demonstrated no sodium deficiency, good performance (120-130 mAh g⁻¹ at C/5) and capacity retention upon cycling (75 % after 100 cycles), as well as a high coulombic efficiency and good rate capability up to a current as high as 10C, hence showing promising results for a possible application in full cell configuration.

References

- [1] Kundu, D.; Talaie, E.; Duffort, V.; Nazar, L.F.; The Emerging Chemistry of Sodium Ion Batteries for Electrochemical Energy Storage. *Angew. Chemie - Int. Ed.* 2015, 54 (11), 3432–3448.
- [2] Peng, J.; Zhang, W.; Liu, Q.; Wang, J.; Chou, S.; Liu, H.; Dou, S.; Prussian Blue Analogues for Sodium-Ion Batteries: Past, Present, and Future. *Adv. Mater.* 2022, 34 (15), 1–20.
- [3] Maddar, F.M.; Walker, D.; Chamberlain, T.W.; Compton, J.; Menon, A.S.; Copley, M.; Hasa, I.; Understanding dehydration of Prussian white: from material to aqueous processed composite electrodes for sodium-ion battery application. *J. Mater. Chem. A* 2023, 11, 15778.
- [4] Gusev, A.; Baluda, Y.; Braga, E.; Kryukova, M.; Kiskin, M.; Chuyan, E.; Ravaeva, M.; Cheretaev, I.; Linert, W.; *Inorganica Chimica Acta* 2021, 528, 120606.
- [5] Wang, P.; Li, Y.; Zhu, D.; Gong, F.; Fang, S.; Zhang, Y.; Sun, S.; *Dalton Trans.* 2022, 51,9622.

Acknowledgments: This work has been financed by the Research Fund for the Italian Electrical System under the Three Year Research Plan 2022-2024 (DM MITE n. 337, 15.09.2022), in compliance with the Decree of April 16th, 2018".