

Effect of Mn and Co interaction in Hexacyanoferrate over electrochemical behavior as cathode in Sodium Ion Batteries

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The Hexacyanoferrate is an open framework material which has the molecular formula $A_xM[P(CN)_6]$, where P is coordinated octahedral to C and M is regularity coordinated octahedral to N, the amount of charge balance cation (A) depend to oxidation state of P and M; particularly this materials is obtained easy by precipitation method, however the synthesized material exhibited lattice vacancies of $[P(CN)_6]^{n-}$ and a low amount of cation within the structure, decreasing its stability during the diffusion of the cation inside the framework[1]; with the aim to minimize this crystalline defects recently has been reported the use of citrate-chelating during synthesis obtained materials with free vacancies and high amount of cation within the structure [2]; as has been reported by Pasta et. al., where the material $NayCo_{1-x}Mnx[Fe(CN)_6]$ was synthesized using an excess of sodium during precipitation, with the purpose to decrease the amount of Co in the framework for obtain a low cost material, however the results reveals that jahn teller distortion exhibited by Mn^{3+} decrease the stability during faradic process in aqueous media.

In this work, Hexacyanoferrates of Co and Mn were synthesized by precipitation method using citrate as chelating agent, the RDX, Raman and Mossbauer reveal the distortion in crystalline cell, the EPR results suggests that the interaction between Mn and Co take place by spin delocalization in Fe center modify the Jahn Teller distortion of Mn^{3+} , which affect the electrochemical stability during charge/discharge process, observed an improved in framework with Mn:Co in equimolar ratio.

References:

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- [2] M. Pasta, R. Y. Wang, R. Ruffo, R. Qiao, H.-W. Lee, B. Shyam, M. Guo, Y. Wang, L. A. Wray, W. Yang, M. F. Toney, Y. Cui, Journal of Materials Chemistry A. 4 (2016) 4211–4223.