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Phase control of Prussian blue analogues for potassium-ion batteries

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There are a lot of studies aimed at replacing lithium-ion batteries (LIB) with sodium-ion batteries (SIB) [1]. Potassium-ion batteries (PIB) are also promising electrochemical devices due to the potassium availability compared to lithium [3]. Unlike sodium, PIBs can use graphite as anode material, suggesting that the well-developed LIB system can be better transferred to the PIB system. Developing efficient cathode materials is an important task for the wide distribution of SIB and PIB. One of the perspective cathode materials are hexacyanoferrates $MxFe[Fe(CN)6] \cdot nH2O$ (Prussian blue analogues, M = Na, K), which have open framework structure and low-temperature synthesis.

A number of samples of KxFe[Fe(CN)6] nH2O were obtained by hydrochloric acid decomposition of potassium ferrocyanide in aqueous solution. The morphology and crystal structure dependence from synthesis conditions was analyzed. In a pure hydrochloric acid solution, cubic particles of the material are formed. The presence of ascorbic and citric acids does not change the morphology of the samples. An addition of the saturated solution of potassium chloride during acid decomposition leads to the formation of shapeless particles of slightly smaller size compared to the synthesis in the HCl solution.

Samples synthesized in the presence of ascorbic acid with argon purging have a chemical composition of K1.83Fe[Fe(CN)6]·nH2O and cubic morphology with particle face sizes up to 2.2 µm. They have monoclinic structure P21/c, stable during heating up to 250 degrees.

[1] G. Du, H. Pang. Recent advancements in Prussian blue analogues: Preparation and application in batteries // Energy Storage Materials 36 (2021) 387–408

[2] Y. Bai et al. Progress of Prussian Blue and Its Analogues as Cathode Materials for Potassium Ion Batteries // Eur. J. Inorg. Chem. 2023, 26, e202300246

Primary authors: PONOMAREVA, Olga (JINR); VASIN, Roman (JINR); SUMNIKOV, Sergey (JINR); KO-RNEEVA, Ekaterina (FLNR of the Joint Institute for Nuclear Research, Dubna, Russia); SAMOYLOVA, Nataliya (JINR FLNP)

Presenter: PONOMAREVA, Olga (JINR)

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