

Synthesis and electrochemical investigation of the mixed phosphate-pyrophosphates
 $\text{Na}_4(\text{Ni}_{1-x}\text{Fe}_x)_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ ($x = 0.25, 0.5$).

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The mixed polyanionic framework structures, as phosphate-pyrophosphates of sodium and 3d-metals (V, Fe, Co, Mn and Ni), are considered as promising cathode materials for sodium-ion batteries due to their superior Na mobility, high operating voltage and thermal stability. The Ni-based cathode material of this family, $\text{Na}_4\text{Ni}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$, attracts an attention due to its high operating working potential (~ 5 V vs. Na/Na^+) and the theoretical capacity of $127 \text{ mAh}\cdot\text{g}^{-1}$ [1]. However, capacity fading of more than 30 % after the 1st cycle hampers the practical application. The substitution in 3d-metal sublattice might enhance the cycling stability due to working potential window shift. This work is devoted to synthesis of Fe-substituted $\text{Na}_4(\text{Ni}_{1-x}\text{Fe}_x)_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ compounds and to investigation of corresponding electrochemical properties.

The single phase samples of the mixed phosphate-pyrophosphates $\text{Na}_4(\text{Ni}_{1-x}\text{Fe}_x)_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ ($x = 0.25, 0.5$) have been obtained via conventional solid state synthesis in argon atmosphere. Both compounds are isostructural to $\text{Na}_4\text{Ni}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ (sp. gr. $Pn2_1a$, $Z = 4$) with corresponding decrease in lattice parameters and volumes: $a = 18.030(1) \text{ \AA}$, $b = 6.5061(1) \text{ \AA}$, $c = 10.4814(1) \text{ \AA}$, $V = 1229.51(2) \text{ \AA}^3$ for $x = 0.25$; $a = 18.0401(2) \text{ \AA}$, $b = 6.5235(1) \text{ \AA}$, $c = 10.5482(1) \text{ \AA}$, $V = 1241.35(3) \text{ \AA}^3$ for $x = 0.5$.

Sodium electrochemical (de)intercalation into $\text{Na}_4(\text{Ni}_{1-x}\text{Fe}_x)_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ have been investigated by cycling voltammetry and galvanostatic charge-discharge using two-electrode cells assembled in argon-filled glove-box with 1 M solution of NaPF_6 in propylene carbonate as electrolyte and sodium metal anode. *Ex situ* X-ray powder diffraction and scanning electron microscopy were used for electrodes characterization.

The CV-curves obtained for $\text{Na}_4\text{Ni}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_2\text{P}_2\text{O}_7$ within the potential range of 2.5–4 V vs. Na/Na^+ revealed three peaks (3.2 V – 3.6 V) with good cycling stability, that is similar to $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ behavior [3], but with higher potentials (3.0 – 3.2 V for the latter). The redox processes correspond to $\text{Fe}^{2+/3+}$ transition with charge capacity of $\sim 60 \text{ mAh}\cdot\text{g}^{-1}$. The extension of the potential range up to 5.1 V vs. Na/Na^+ resulted in appearance of three additional peaks (4.1 – 4.6 V), with the potentials lower than ones for pure $\text{Na}_4\text{Ni}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$. This process, attributed to Ni oxidation, was not reversible.

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References:

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