

KTiPO₄F and α -TiPO₄ as electrode materials for metal-ion batteries

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Nowadays, 3d-metal phosphates are considered as promising electrode materials for metal-ion batteries (MIB). A phosphate group increases working potential of the M^{n+1}/M^{n+} redox pair and provides higher electrochemical and thermal stability that contribute to a longer life of electrodes up to several thousand charge/discharge cycles. Typically titanium redox transitions are not used for cathode applications because of low operating potential. Among titanium transitions Ti^{4+}/Ti^{3+} and Ti^{3+}/Ti^{2+} , the latter is supposed to demonstrate a lower working potential which is preferable for anode materials, however, due to the side conversion reactions, such examples are extremely rare. The d^1 electronic configuration of titanium (III) compounds is more preferable due to the higher electronic conductivity. Titanium reagents are comparable in cost with those of manganese, are produced widely and everywhere, non-toxic, and can be easily recycled, making titanium an attractive element for the industry.

Recently, our research group has developed several Ti(III) fluoride phosphates. One of them, KTiPO₄F, adopting the KTiOPO₄ (KTP)-type structure is a new compound, which was obtained in one stage via hydrothermal synthesis. Since, potassium and ammonium cations have the near ionic radius and crystallize in the same KTP structural type during the hydrothermal reaction, a new composition NH₄TiPO₄F can be prepared using ammonium salts by the same way as KTiPO₄F. Moreover, the similarity between the KTP and α -CrPO₄ structural types which enabled preparation of a new TiPO₄-compound with the α -CrPO₄ structure during the thermal decomposition of NH₄TiPO₄F.

Electrochemical investigation has shown the reversible activity of the KTiPO₄F/C electrode material in the potassium half-cell in the potential range from 2.0 to 4.0 V vs. K⁺/K. For the Ti^{4+}/Ti^{3+} couple, anomalously high potentials of the de/intercalation process were observed, reaching 3.6 V vs. K⁺/K, that can be explained by a combination of structural effects, as well as the inductive effect of the phosphate and fluorine-anionic groups. It should be noted that 3.6 V is still the record value of K⁺ de/intercalation for Ti^{4+}/Ti^{3+} redox transition. α -TiPO₄ shows reversible de/intercalation of Li⁺ at specifically high potentials for this Ti^{3+}/Ti^{2+} couple.

The report will consider in detail the peculiarities of hydrothermal synthesis of new Ti^{3+} -containing compounds, the regularities of phase formation in the KTiPO₄F and α -TiPO₄ systems, as well as a detailed analysis of mechanisms of electrochemical de/intercalation of ions in the structure of the studied compounds.

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