$Li_3V_2(PO_4)_3$-based composites as potential cathode materials for lithium-ion batteries: ESR measurements

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Compounds based on lithium-vanadium phosphate $Li_3V_2(PO_4)_3$ can be used as a cathode material in metal-ion batteries due to the stability of their crystal structure with respect to the change in the valence state of transition ion caused by the processes of intercalation/deintercalation of an alkaline element during the charge/discharge process of the electrochemical cell, so the investigation of physical properties of $Li_3V_2(PO_4)_3$-based structures is of great interest. Here we present the investigations of magnetic and electrochemical properties of $Li_3V_2(PO_4)_3$-based composites, including $Li_3V_2(PO_4)_3/Li_3PO_4$ (LVPO/LPO) and $Li_3V_2(PO_4)_3$/C (LVPO/C).

LVPO/LPO solid solutions were obtained by the thermal hydrolysis method [1] or hydrothermal method with the subsequent annealing in Ar atmosphere. In comparison, the mesoporous sample of LVPO/C was synthesized by the soft-template method [2]. Investigations of electrochemical properties showed the discharge capacity retention after hundred charge/discharge cycles for all samples and an increase in the discharge capacity in LVPO/LPO composite with an increase in lithium deficiency.

Magnetic properties of LVPO/LPO and LVPO/C composites were investigated using magnetometry and electron spin resonance (ESR) methods. As-prepared samples demonstrated the paramagnetic properties due to the presence of V^{4+} ions ($3d^1$, S=1/2) because of non-stoichiometry (lithium deficiency) of the sample. The degree of non-stoichiometry depends on the composition of the sample (including the amount of Li_3PO_4 salt) and its increasing is accompanied by an increase in the amount of V^{4+} ions that can be directly detected using the ESR method. ESR measurements of lithiated and delithiated LVPO/C samples showed the complete reduction of vanadium ions to the valence state V^{3+} after the first charge/discharge cycle indicating the reversible intercalation of all lithium ions to the structure during the first delithiation/lithiation cycle in the investigated composite.

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[2] T.P. Gavrilova, S.M. Khantimerov, et al., *Solid State Commun.* **2021**, *323*, pp. 114108 1 – 6.