

Mixed Niobium Phosphates as Negative Electode Materials for Metal-ion Batteries

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With the rapid development of electric vehicles and energy storage devices safety and powerful requirements to metal-ion batteries becomes apparent. Niobium-containing compounds [1] attracts attention of researchers as negative electrode materials due to their ability to multielectron reactions. They are important for achieving high capacity. High columbic efficiency on first cycle, rate capability and safety are main benefits of Nb-containing anode materials, which distinguish them against the carbon materials, however, there are only a few recent works that are devoted to investigation of niobium phosphates as electrode materials [2,3]. Electrochemical activity of mixed niobium-vanadium phosphates has not been studied yet. Potential of V^{3+}/V^{2+} is located between $Nb^{5+/4+}$ and $Nb^{4+/3+}$ potentials [4], this way three electron red-ox process in low potential area can be achieved.

The aim of this work is research of multielectron redox processes in mixed niobium-vanadium phosphates with NASICON-related structures.

$LiNbV(PO_4)_3$ (*Pbcn*) and $NaNbV(PO_4)_3$ (*R-3c*) were synthesized by sol-gel method, cell parameters of both phases are in agreement with literature data [5]. This method helped us to reduce synthesis temperature and obtain particles with lower size, than once received via solid state route [2]. Morphology is very important for further electrochemical measurements. *Operando*-XANES spectroscopy of $LiNbV(PO_4)_3$ and $NaNbV(PO_4)_3$ proved, that in initial phase oxidation state of Nb is +5. Shift of Nb K-edge during the intercalation processes indicates Nb reduction deeper than Nb^{+4} . Capacity is very close to theoretical, in combination with XANES data it allows us to speculate about the intercalation of 3 alkali cations per formula unit. $NaNbV(PO_4)_3$ demonstrates excellent rate capability up to 10C (more than 80% of theoretical capacity) and good cycling stability (less than 7% capacity fade after 100 cycles) [6].

Operando and *ex situ* XRD proved that intercalation processes in both phases are reversible. For $LiNbV(PO_4)_3$ lithation proceeds with single-phase mechanism, with increasing of parameters *a* and *c* and decreasing of parameter *b*. Data analysis obtained from $NaNbV(PO_4)_3$ *operando* XRD showed the existence of two-phase regions and nonmonotonicity in changing *c* parameter which can be related to activity of different redox processes at different potentials.

Combination of mild chemistry methods and activity of three redox couples allowed to synthesize negative electrode material for high power and long-life metal-ion batteries.

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