Novel vanadium-based phosphates as sodium-ion battery positive electrodes

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The realization and commercialization of sodium-ion batteries vastly relies on the advances in positive electrode materials having superior electrochemical properties [1]. Among the existing materials, there is a competition between oxide and polyanion families: while the former averagely display higher capacities and energy density, the latter show unprecedented long-cycling stability and power characteristics. Moreover the polyanion materials possess a rich variety of structural types that provides a huge playground for designing new materials with unique properties.

In this work, we offer a new class of positive electrode materials designed by merging a promising $NaVPO_4X$ (X = F, O) chemical composition and a high-rate $KTiOPO_4$-(KTP)-type structural framework with promising transport properties. This fusion is enabled by a devised low-temperature synthesis approach composing of two stages: hydrothermal treatment and chemical ion-exchange reaction. Being superior to most of the renowned Na-based cathodes, these electrode materials exhibits steady high-voltage and high-power electrochemical performance. Depending on the X the materials deliver up to 130-135 mAh g^{-1} of reversible capacity (more than 90% of the theoretical values, Figure 1) at a C/10 rate at average discharge potentials of 3.7-4.0 V vs. Na^+/Na (depending on the X). At higher rate of 10C the materials show up to 100 mAh g^{-1} (with high loading of 22 mg cm^{-2} of active material, equal to 3 mAh cm^{-2}). The de/intercalation and charge compensation mechanisms of the materials were studied by operando and ex situ XRD and XAS techniques. The fluoride phosphate representative follows mostly an advantageous solid-solution mechanism, whereas turning to oxophosphate brings about several minor phase transitions possibly associated with charge ordering in the lattice. From a practical point of view, the materials validate their commercial elegibility in steady-functioning 4 V hard carbon-anode-based full cells. Overall, KTP-type $NaVPO_4X$ phosphates unravel the practical specific energy of in the range of 480-540 Wh kg^{-1} setting a new standard for the polyanion Na-ion battery positive electrodes.

In the presentation, different aspects of synthesis, crystal structure refinement, materials characterization and electrochemical properties of these new KTP-type phosphate cathode materials will be presented with particular attention to the composition-structure-property relationships; as well as de/intercalation and charge compensation mechanisms studied by ex situ and operando XRD/XAS. A special emphasis will also be given to the place of KTP-$NaVPO_4X$ among the multitude of polymorphs and closely-related cathode materials.

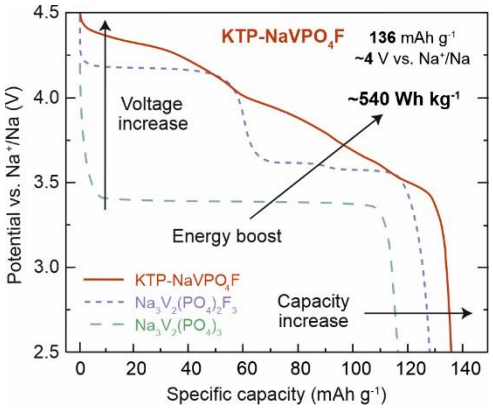

Figure 1. Potential vs. specific capacity plots for $Na_3V_2(PO_4)_3$, $Na_3V_2(PO_4)_2F_3$, normalized to the theoretical specific capacity per one-electron $V^{3+}\leftrightarrow V^{4+}$ transition. For KTP-$NaVPO_4F$, the experimental discharge profile is presented for comparison..

References

[1] A. M. Abakumov, S. S. Fedotov et al Nat. Commun. 11 (2020) 4976.

[2] S. D. Shraer, N. D. Luchinin, et al Nat. Commun. 13 (2022) 4097.

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