# NEW POLYMORPHS OF $A_xMPO_4F$ FLUORIDE PHOSPHATES AS CATHODE MATERIALS FOR RECHARGEABLE BATTERIES

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In the pursuit of low-cost, eco-friendly and chemically stable cathode materials, a huge variety of candidates was thoroughly inspected starting from layered oxides to complex polyanion and mixed anion compounds. At the same time the crystal structure of the cathodes have evolved from close packages into much more sophisticated arrangements, which opened up opportunities to tune the electrochemical properties of the resulting electrode materials. Fluoride phosphates based cathode materials with $A_xMPO_4F$ general formula (x = 1, 2; A – alkali metal; M – 3d transition metal)[1,2,3] are in focus due to the several advantages arising from the combination of phosphate and fluoride anion moieties as well as the richer structural diversity. The phosphate group is responsible for a structural, chemical and thermal stability; the fluoride anion anticipates a better kinetics of the mobile ion and brings about an increase of the working potential.

Within the scope of this work we investigated mixed $(Li,Na)_2Co_{1-x}M_xPO_4F$ (M = Mn, Fe) and $AVPO_4F$ fluoride-phosphates as cathode materials for Li-ion batteries and found two new polymorphs crystallizing in the orthorhombic system with quasi-2D and 3D frameworks respectively. A freeze-drying assisted ceramic route was applied to the synthesis of the materials, which allowed lowering sintering temperatures and stabilizing new structural modifications. The crystal structure was studied by X-ray, electron and neutron diffraction, chemical composition was verified by TEM-EDX and ICP-AES methods. The materials were tested in Li-anode cells by galvanostatic cycling and voltammetry techniques. The new polymorphs demonstrated a reversible electrochemical activity in 2.0÷4.8 V potential range with good capacity retention and high rate capability up to 40C preserving more than 50% of the theoretical specific capacity. Composition-structure-property relationships in these fluoride-phosphate systems will be discussed with a special focus to the interrelation between structure peculiarities and electrochemical properties.

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