

m40.p01

Computational investigations on fluorinated-polyoxyanionic compounds as cathode materials for lithium batteries

E.M. Arroyo y de Dompablo^a, U. Amador^b, J.-M. Tarascon^c

^aDept. Química Inorgánica Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid. ^bDpt. Química, Fac. Farmacia, Universidad San Pablo-CEU, 28668 Boadilla del Monte, Madrid, Spain. ^cL RCS, Université de Picardie Jules-Verne, UMR 6007 CNRS, 33 rue Saint-Leu, 80039, Amiens, France. E-mail: e.arroyo@quim.ucm.es

Keywords: lithium batteries, crystal structure prediction, ab initio calculations

The chemistry of fluorinated compounds is getting increasing relevance in the field of lithium battery materials. Barker *et al* reported that the V^{+3}/V^{+4} redox couple in the cathode material $LiVPO_4F$ operates at 4.01 V, which is 0.3 V above its operation voltage in $Li_3V_2(PO_4)_3$ [1], suggesting the idea that fluorophosphates display a higher voltage than related phosphates. To investigate the effect that fluorine substitution might have on the electrochemical properties of polyoxyanionic compounds, we have performed a first principles study on three fluorinated polyoxyanionic systems: the above mentioned $LiVPO_4F$, layered- $LiVSiO_4F$ and olivine- $Li_{0.5}FePO_{3.5}F_{0.5}$. A computational investigation allows working at a fix composition while keeping a full control over the structure, hence making it possible to select a particular crystallographic site to be occupied by the substituting fluorine anions. In this communication we will show that the effect of the fluorine ion on the lithium insertion voltage, and in a greater extend over the general electrochemical behavior, depends on the particular crystallographic site that it occupies in the polyoxyanionic structure.

[1] Barker J., Saidi M.Y., Swoyer, J.L., *J. Electrochem. Soc.*, 2003, 150, 1394.

m40.p02

Synthesis and Properties of Solid Solutions in One-Layer Aurivillius Phases

Elena Kharitonova, Valentina Voronkova, Olga Rudnitskaya

Faculty of Physics, M.V. Lomonosov Moscow State University, Russia. E-mail: harit@poly.phys.msu.ru

Keywords: superionic materials, solid solutions, structure and properties

The series of polycrystalline solid solutions in $Bi_2VO_{5.5}(BV)$ - $Bi_2GeO_5(BG)$, $Bi_2VO_{5.5}(BV)$ - $Bi_2MoO_6(BM)$ and $Bi_2VO_{5.5}(BV)$ - $Bi_2WO_6(BW)$ systems have been synthesized and their polymorphism, ferroelectric and oxide conductive properties have been investigated in 30 - 960°C temperature region. The restricted solid solutions on the base of BV, BM and BW exist in the last two systems in contrast to BV-BG, where the complete solid solutions have been observed.

The BV-BG system is very sensitive to their prehistory. The increase of Ge content leads to decrease of orthorhombic distortion. In the region 40 - 60% Ge the tetragonal phase is stabilized. At the further increasing of Ge content the orthorhombic phase appears again. The conductivity of solid solutions smoothly falls in all temperature region with increasing of Ge content.

The BM-BV system is found to be non-binary and to be one cut in the ternary system with restricted BM and BV based solid solutions in the region 0 - 10% V or Mo content respectively. The increasing of conductivity in BM based solid solutions have been observed. The conductivity of BV based solid solutions changes little.

In the BV-BW system solid solutions in the range 0 - 20% W and 0 - 25% V exist. The increasing of W content up to 16% stabilizes the tetragonal phase in BV based solid solutions. The conductivity of tetragonal phase reaches 0.3 S/cm at 550°C. The conductivity of BW based solid solutions increases with increase of V content.

This work is supported by RFBR (grant No. 04-03-32434).