Iron substituted lithium titanium spinels as negative electrodes for lithium ion batteries

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Iron substituted lithium titanium spinels with stoichiometry $Li_{4/3-x/3}Fe_xTi_{5/3-2x/3}O_4$ were synthesized by sol gel process, using lithium acetate $CH_3COOLi{\cdot}H_2O$, titanium isopropoxide $Ti(OCH(CH_3)_2)_4$ and iron nitrate $Fe(NO_3)_3{\cdot}9H_2O$ in ethanol.
The attention was focused on two compositions, namely $Li_{1.3}Fe_{0.1}Ti_{1.6}O_4$ and $Li_{1.25}Fe_{0.25}Ti_{1.5}O_4$. In the first case, for x=0.1, the spinel crystallizes in the typical $Fd\bar{3}m$ space group while in the latter case, for x=0.25 it adopts the $P4_332$ symmetry [1].

The materials were tested as negative electrodes for lithium ion batteries. It was observed that these materials are capable to insert up to 1.4-1.6 lithium ion equivalents per formula unit and to cycle reversibly 160-180mAh/g at C/5 in the 2.9-0.2V potential range.

The insertion processes were studied, as reported in previous works [2-7], by combining electrochemical tests with in situ diffraction measurements carried out at the high energy beam line of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.

The two spinels showed an electrochemical response that is quite different from the pure $Li_{4/3}Ti_{5/3}O_4$, since the insertion (deinsertion) process seems to evolve through several one-phase and two-phases domains, clearly involving the reduction (oxidation) of both the titanium (IV) and the iron (III) which occupy different framework positions [8].

Slight differences in stoichiometry and in symmetry originate little changes in the voltage profile, the trend remaining in average similar.

Three plateau are present in the first discharge curve (Figure 1): an irreversible process at around 2.2V vs Li^+/Li, and two reversible plateau at 1.5 and 0.5V vs Li^+/Li. During the recharge only one plateau develops around 1.6V. This plateau is believed to be connected to both the 1.5 and 0.5V discharge processes. The redox process around 1.5V is attributed to the Ti^{4+}/Ti^{3+} redox couple. It is a two phase process involving the migration of cations from the tetrahedral to the octahedral position in order to allow the insertion of lithium inside the spinel framework. The irreversible 2.2V insertion process is believed to be related to the Fe^{3+}/Fe^{2+} redox couple and to an initial monophasic insertion into the spinel framework. The low voltage plateau should be due to further reduction to metal iron and to the formation of a defective rocksalt structure. The overall structural strain was measured to be less then 1%. The x-ray diffraction pattern evolution collected during galvanostatic cycles, as reported in figure 2, will be discussed [9].

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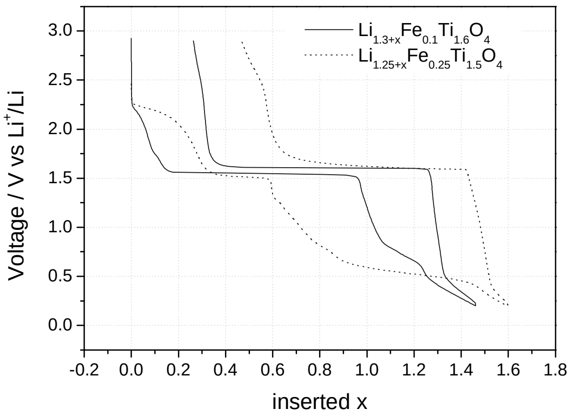

Figure 1: Voltage profile of the first potentiodinamic cycle with galvanostatic acceleration for the two spinel electrodes. $LiClO_4$ EC:DEC electrolyte; Li reference.

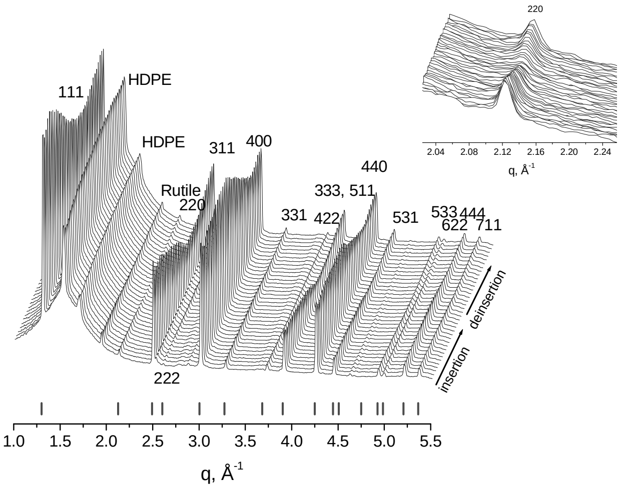

Figure 2: X-ray diffraction patterns collected during the first galvanostatic cycle (2.9-1.2V) of a $Li_{1.3+x}Fe_{0.1}Ti_{1.6}O_4$ electrode. The 220 peak is reported in detail.