Near Heterosite Li$_{0.1}$FePO$_4$ Phase Formation as Atmospheric Aging Product of LiFePO$_4$/C Composite. Electrochemical, Magnetic and EPR Study

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Freeze-drying method was employed in order to synthesize a LiFePO$_4$/C composite. This method produced phosphate nanoparticles (10–20 nm size) covered in a carbon network. Nanostructuring and homogeneous conductive web around the active material promoted a good electrochemical response, with 141 mAh·g$^{-1}$ at C/1 and a capacity retention of 90% up to 300 cycles. However, XRD measurements showed the presence of an approximately 30% of a near heterosite Li$_{0.1}$FePO$_4$ intermediate phase in the initial sample, as a product of atmospheric aging. EPR spectrum displayed a very broad signal attributed to a high spin Fe$^{3+}$ ion magnetically coupled to Fe$^{2+}$, confirming the formation of the non stoichiometric Li$_x$FePO$_4$ compound. Electrochemical measurements indicated the presence of active Fe$^{3+}$ in the initial composite, in a structural environment close to that of a FePO$_4$ heterosite system. A post-mortem cathode, stopped at 4 V, was characterized. Metastable Li$_x$FePO$_4$ solid solution type phase was not noticed. Thus, it would have disappeared during cathode cycling life, and all active material would have evolved to a classic biphasic system.© 2011 The Electrochemical Society. [DOI: 10.1149/1.3611435] All rights reserved.