

Investigation of the electrode / electrolyte interphase for Air-Exposed LiFePO₄ Nanopowders

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The olivine-type compositions LiMPO₄ (M = Fe, Mn, Co) are among the most attractive materials for the positive electrode of Li-ion batteries, and now stand as a good choice for power tools and hybrid vehicles. Interfacial reactions and the growth of a passivation layer at the electrode surface upon cycling have been also highlighted for different positive electrode materials and have proven of paramount importance as they can lead to performance degradation of the battery upon aging and cycling [1, 2]. The conditions in which degradation processes at the positive electrode / electrolyte interface occur are still incompletely understood [3, 4] and need further investigation. The purpose of the present work is to shed light on the surface reaction mechanism of LiFePO₄ in air, on the characterization of the resulting surface side phase(s) and on their consequence on battery performance.

Prolonged atmosphere contact at room temperature leads to the formation of a disordered Fe^{III}-rich side phases and cell volume shrinkage [5, 6]. Structural and electrochemical characterization indicate that the amorphous ferric phosphate formed in the early aging stage exhibits favorable composition and structure at the local scale, preceding the crystallization of proper favorable LiFePO₄(OH). The presence of these surface ferric phases, even for early stage of the aging process, leads not only to a significant decrease of the capacity available in a Li-ion configuration but also to a complex electrochemical activity, including a significant irreversible reaction with electrolyte involving possible soluble species.

The Li battery behavior of the pristine and altered materials has been studied. The effect of the electrolyte degradation and the deposit of

species on the positive electrode surface have been followed by XPS, In-situ Impedance Spectroscopy and NMR (⁷Li, ¹⁹F, ³¹P) upon cycling. Widely considered as chemically inert toward the electrolyte, LiFePO₄ actually exhibits a complex, dynamic interaction with classical LiPF₆ / EC:DMC solution. Solvents are degraded on LiFePO₄ surface at high potentials and their decomposition products form a SPL type interphase that subsequently dissolves at lower potentials. For an air-aged LiFePO₄, the chemisorbed/incorporated water or hydroxyl groups seem to favor the dissolution of the LiFePO₄ upon contact with the electrolyte or cycling.

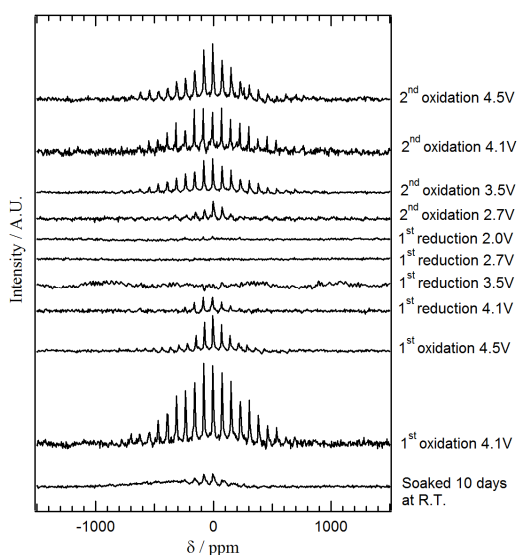


Figure 1: ⁷Li MAS NMR Spectra for the composite LiFePO₄-C along the first galvanostatic cycle at C/10 in LiPF₆ EC:DMC at room temperature.

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