Surface Film Formation on $Li_xMn_2O_4$ Electrodes

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$LiMn_2O_4$ is ideal as a high-capacity Li-ion battery cathode material by virtue of its low toxicity, low cost, and the high natural abundance of Mn. Surface related reactions have been the major focus of this work. The main techniques exploited have been: constant current electrochemical cycling, X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (FTIR), X-ray diffraction (XRD) and thermal analysis (DSC).

Interface formation between the $LiMn_2O_4$ cathode and carbonate-based electrolytes has been followed under different pre-treatment conditions. The variables have been: number of charge/discharge cycles, storage time, potential, electrolyte salt and temperature.

It was found that the formation of the surface layer was not governed by electrochemical cycling (Fig. 1).The species precipitating on the surface of the cathodes at ambient temperature was determined to comprise a mixture of organic and inorganic compounds: LiF, Li_xPF_y (or Li_xBF_y, depending on the electrolyte salt used), $Li_xPO_yF_z$ (or $Li_xBO_yF_z$) and poly(oxyethylene). Additional compounds were found at elevated temperatures: phosphorus pent-oxides (or boron oxide) and polycarbonate. A model will be presented for the formation of these surface species at elevated temperatures.

The cathode surface structure was found to change towards a lithium-rich and Mn^{3+}-rich compound under self-discharge. The reduction of $LiMn_2O_4$, in addition to the high operating potential, promotes oxidation of the electrolyte at the cathode surface.

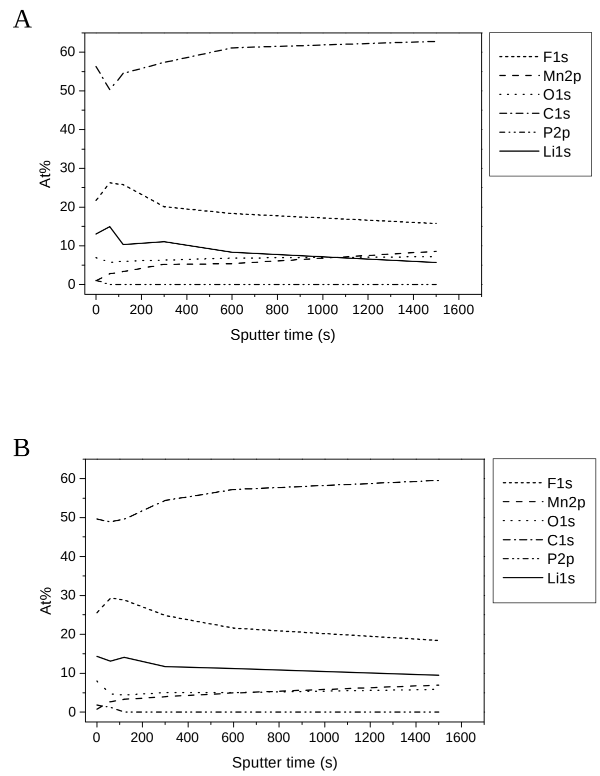

Figure 1. XPS depth profiles of $LiMn_2O_4$ electrodes in $LiPF_6$ electrolyte at room-temperature. A. 50 cycles at C/3. B. Stored at open-circuit potential for 300h.