

Evidence of a Cationic Substitution Domain in Lithium-Manganese Spinel

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Magnetic susceptibility measurements and electron paramagnetic resonance spectra of samples prepared from the reactive system $\text{MnO}/\text{Li}_2\text{CO}_3$ with different starting Li cationic fraction x are analyzed, taking into account the structural and compositional information provided by x-ray diffraction. Parent phases, as Mn_2O_3 , Mn_3O_4 and Li_2MnO_3 , arise together with the lithium-manganese spinel as a result of Li-deficiency or Li-excess with respect to the $x = 0.33$ composition pertinent to the stoichiometric LiMn_2O_4 spinel. The data show that the spinel phase can sustain a partial Li-Mn substitution in the cation sites, according to compositional models described, for $x > 0.33$, by $\text{Li}_{1+y}\text{Mn}_{1-3y}^{3+}\text{Mn}_{1+2y}^{4+}\text{O}_4$ (Li-rich spinel) and, for $x < 0.33$, by $\text{Li}_{1-|y|}\text{Mn}_{|y|}^{2+}\text{Mn}_{1+|y|}^{3+}\text{Mn}_{1-|y|}^{4+}\text{O}_4$ (Li-poor spinel). Paramagnetic resonance data of the Li-poor spinel phase are analyzed to discuss the possible oxidation state of Mn in the tetrahedral site.

Key words: Stoichiometric LiMn_2O_4 Spinel Phase, Magnetic Susceptibility, Electron Paramagnetic Resonance.

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