Evidence of a Cationic Substitution Domain in Lithium-Manganese Spinels

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Magnetic susceptibility measurements and electron paramagnetic resonance spectra of samples prepared from the reactive system MnO/Li\textsubscript{2}CO\textsubscript{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\textsubscript{2}O\textsubscript{3}, Mn\textsubscript{3}O\textsubscript{4} and Li\textsubscript{2}MnO\textsubscript{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\textsubscript{2}O\textsubscript{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 Li\textsuperscript{1+}\(_{y}\)Mn\textsuperscript{3+}\(_{1-y}\)Mn\textsuperscript{4+}\(_{2y}\)O\textsubscript{4} (Li-rich spinel) and, for \(x < 0.33\), by Li\textsuperscript{1+}\(_{-y}\)Mn\textsuperscript{2+}\(_{y}\)Mn\textsuperscript{3+}\(_{1+y}\)Mn\textsuperscript{4+}\(_{-y}\)O\textsubscript{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.

\textit{Key words:} Stoichiometric LiMn\textsubscript{2}O\textsubscript{4} Spinel Phase, Magnetic Susceptibility, Electron Paramagnetic Resonance.

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