Effect of doping of lithium manganese spinel on manganese solubility in liquid electrolyte

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Idea of future world without fossil fuels raise interest in the field of rechargeable batteries due to applications in electric vehicles (EV), renewable energy storage systems as well as space and military technology. Manganese based materials may be recipe for new tomorrow as its compounds offer attractive characteristics of low cost, environmental benignity, abundance, and high intrinsic mass density. Among many other cathode materials lithium manganese spinel ($LiMn_2O_4$, LMO) has been considered as one of the most promising for use in EV's batteries. [1]

Despite desirable features offered by LMO and its derivatives, major drawbacks need to be eliminated before it will be possible to increase the share of manganese-based materials in the battery market. This type of materials have tendency to degrade upon electrochemical work, leading to power fading and irreversible capacity loss of the battery cell. Several phenomena affecting cell performance have been proposed. Firstly phase transition at room temperature inciting lattice stress and structural instability is one of the complications that occurs. Another is formation of surface-dependent solid-electrolyte interfaces (SEI) from electrolyte decomposition. Other can be Jahn-Teller distortion of Mn^{3+} ions. But main problem is associated with manganese disproportionation reaction ($2Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+}$) and subsequent dissolution of Mn^{2+} ions in liquid electrolyte. These processes ultimately lead to the loss of active material and deposition of Mn species on negative electrode as well as worsening of electrolyte performance. [2]

Herein, LMO and lithium manganese spinel doped with sulphur ($LiMn_2O_{3,99}S_{0,01}$, LMOS) cathode materials [3] were studied in order to analyse kinetics of manganese solubility in liquid electrolyte. Lithium hexafluorophosphate solution in ethylene carbonate and dimethyl carbonate (1.0 M $LiPF_6$ in EC/DMC 50/50 v/v) was used as electrolytic conductor as it is considered standard for investigated materials. [4] Sulphur doping effect on the manganese solubility has been verified. Moreover, influence of different temperatures in which electrochemical cell can be used were checked. Both aspects were measured via Electrothermal Atomic Absorption Spectrometry (ET-AAS).

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