

On the Consequences of Manganese Dissolution in Li-Ion Batteries

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One of the main routes for performance degradation (primarily manifested as capacity fading) in Li-ion batteries is initiated by the dissolution of transition metal cations (manganese II from spinel LiMn_2O_4 or mixed manganese containing oxides, iron II from LiFePO_4) from the positive electrode. These ions will migrate to the negative electrode and contaminate its surface. There they cause the catalytic decomposition of solvent molecules, which will lead to the degradation of battery performance. It is believed that Mn deposited on or in the immediate vicinity (the SEI layer) of the graphite particles in the negative electrode is the main source for the performance degradation and, therefore, that the deposition of a nanometer-scale inorganic barrier films on the negative electrode (e.g., Al_2O_3) as artificial SEI can prevent the deleterious effects ensuing from the Mn deposition on graphite. We challenge this view of Li-ion battery performance degradation and proposed mitigation measure. We will show that *Mn situated anywhere in a Li-ion battery* (i.e., not only on or in the immediate vicinity of the graphite in the negative electrode, and not necessarily within the tunneling distance of electrons from the electronically conductive carbon black filler or graphite particles in the negative electrode) *will impair Li-ion battery performance*. We will present results on the performance of polymeric forms of aza-15-crown-5 and aza-18-crown-6 as chelating agents for Mn^{2+} cations in graphite- $\text{Li}_x\text{Mn}_2\text{O}_4$ cells, obtained from galvanostatic cycling at 60°C, X-ray fluorescence, XPS and NMR experiments that substantiate our conclusion-