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Lithium manganese oxide spinels with substitution of certain metals for the manganese have been the subject of much interest as cathode materials for lithium rechargeable batteries.<sup>1-3</sup> This work attempts to elucidate the performance-improving effects that metal substitution has on the spinel structure by coupling MAS-NMR and electrochemical studies.

Substituted spinels, LiM<sub>y</sub>Mn<sub>2-y</sub>O<sub>4</sub> (0 < y < 0.25, M=Li, Ni, Zn, Co, Al, Cr), have been prepared at 850°C (600°C for M=Li) in flowing oxygen. Selected compositions have been cycled vs. lithium foil on the 4-volt plateau. All substituted compositions show improved capacity retention relative to LiMn<sub>2</sub>O<sub>4</sub>, with Cr-substitution resulting in the most improvement.

An attempt is made to uncouple the simultaneous processes that occur during electrochemical cycling by subjecting the spinel to certain exaggerated model processes. It is expected that this will elucidate the changes introduced into the spinel structure upon repeated cycling, and the role of the substituting metals in suppression of cycling-induced degradation. The types of damage introduced by the model processes are used to explain the changes observed with NMR after many electrochemical cycles.

The model processes studied here lead to specific changes in the NMR spectra of the damaged electrode. For instance, water damage, overdischarge, and cation mixing on the 16c site all lead to new peaks at lower shifts, due to electrolyte byproducts, a new tetragonally-distorted spinel phase, and octahedrally-coordinated lithium, respectively. No new peaks are observed for LiMn<sub>2</sub>O<sub>4</sub> cycled many times, ruling out these processes as significant contributors to cycling-induced damage. Long-term cycling does, however, lead to a reduction in the lithium intensity, and a broadening of the residual MAS linewidth for spinels that show considerable capacity fade. Similar effects are seen for LiMn<sub>2</sub>O<sub>4</sub> held at high potentials, suggesting electrolyte oxidation at the spinel surface may play a large role in the damage occurring during cycling. The relationship between electrolyte oxidation and capacity fade will be explored for various substituted spinels. The quantitative nature of the NMR experiment will also be exploited to make an estimate of the amount of electrochemically sequestered lithium (that lithium which remains in the spinel and is observed with NMR, but does not contribute to the reversible capacity).

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