

Lithium Magic-Angle Spinning Nuclear Magnetic Resonance Studies of Layered Composite $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ ($\text{M}=\text{Mn, Ni, Co}$) Cathode Materials for Li-ion Batteries: the effect of molten salt flux synthesis. Tetiana Nosach, Mallory Gobet, Steve Greenbaum, Hunter College of CUNY, New York, NY 10065; Edwin Ortiz-Quiles, Jessica Soler, William West Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109

Solid-state nuclear magnetic resonance (NMR) spectroscopy was employed to obtain detailed information on lithium environments for $\text{Li}_2\text{MnO}_3\text{:LiMO}_2$ ($\text{M}=\text{Mn, Ni, Co}$) compounds. These layered-layered composites have applications as cathodes materials in lithium battery industry due to their high specific capacity¹. However, electrodes prepared with this composite oxide provide comparatively low cycle life and poor rate capability particularly at reduced temperature². In these studies we used both ^7Li and ^6Li magic-angle spinning (MAS) NMR to understand the effect of molten salt fluxes on the synthesis of these cathodes materials. The molten salt process has been shown to be a facile, and in principle highly scalable, low-cost method to prepare the class of $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ high specific capacity lithium-ion battery cathodes. We report here on the effect of LiCl as a flux during co-firing of the parent compounds, which leads to much improved electrochemical performance.

Although ^7Li has the much higher natural abundance (93%) and gyromagnetic ratio, ^6Li , characterized as magnetically dilute with a much smaller quadrupole moment, can yield highly resolved spectra that are easier to interpret, particularly in paramagnetic compounds. NMR spectra for the starting materials (parent compounds) in $\text{Li}_2\text{MnO}_3\text{:LiMn}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{O}_2$, were obtained and are consistent with previously reported results^{3,4}. The sample fired at 800°C without LiCl flux is similar in appearance to the Li_2MnO_3 starting material while a significant change in the NMR spectra after the molten LiCl salt treatment was observed. In particular, the spectrum for the untreated sample shows three isotropic shifts at 0 ppm, 700ppm and 1400ppm, which are associated with a diamagnetic LiCoO_2 -like environment (or a diamagnetic impurity), Li-ions residing in the Li-layers, and in the Mn-layers, respectively.

After LiCl treatment, in addition to these 3 environments, a new site centered around 500 ppm can be seen (Figure1). To identify this supplementary site ^6Li MAS NMR with different spinning speeds were performed. The spinning sideband manifold also provided information of the coordination symmetry for lithium environments.

The NMR data strongly suggest that the post-fired $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ with LiCl flux forms a true solid solution rather than a phase separated nanocomposite, given that the latter should likely retain similar Li environments to those of the parent compounds. The Li site distribution suggests a disordered Li environment, which is likely due to the interdiffusion of Li between the previously distinct phases of the parent compounds. This distribution is correlated with enhanced electrochemical performance.

References:

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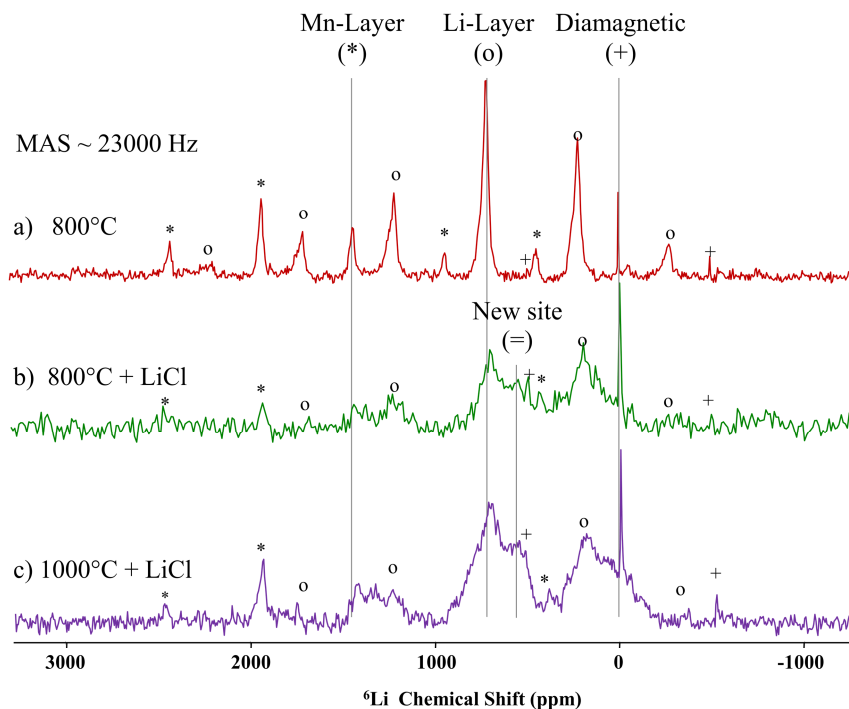


Figure1. ^6Li MAS NMR spectra at 23 kHz of the $\text{Li}_2\text{MnO}_3\text{:Li}[\text{Ni}_{x/3}\text{Mn}_{x/3}\text{Co}_{1/3}]\text{O}_2$ a) after firing at 800°C with no LiCl flux, b) after firing at 800°C with LiCl flux, c) after firing at 1000°C with LiCl flux.