

### Studies of Ion Dynamics in Cathode Materials for Lithium Ion Batteries using Solid-State NMR

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With the rapid development of new technology comes the need for high-energy battery solutions that are both economically and environmentally friendly. In particular the improvement of lithium ion battery components has been driven by their implementation in larger scale applications such as electric vehicles. Specifically the positive electrode (cathode) material has been widely studied in order to identify a candidate that is economically viable, environmentally benign and electrochemically stable.<sup>1</sup>

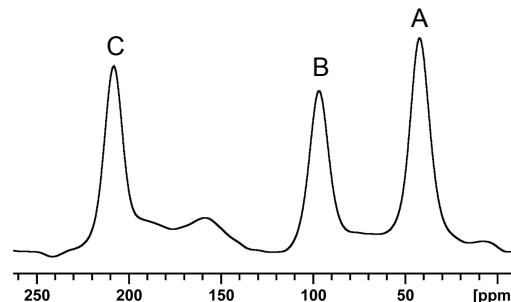
Polyanion frameworks such as phosphates or sulphates have been shown to demonstrate high thermal stability relative to their oxide counterparts.<sup>2,3</sup> A number of fluorinated polyanionic materials have also been studied in an attempt to increase redox potential as well as access novel structures and optimize electrochemical performance.<sup>4,5</sup>

Solid-state nuclear magnetic resonance (NMR) is an ideal method for studying materials in electrochemical systems as it not only allows us to probe the structural framework, but it is also sensitive to the local dynamics of the mobile ion. A variety of NMR techniques have been implemented in order to study Li<sup>+</sup> dynamics, among which include 2D Exchange Spectroscopy (2D EXSY), Selective Inversion (SI) and Rotational-Echo Double-Resonance (REDOR) experiments.

The monoclinic family of Li<sub>3</sub>M<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (M=V, Fe) materials has received significant attention due to their favourable economical and environmental properties while maintaining a high theoretical capacity.<sup>3, 6</sup> Monoclinic Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> was investigated using <sup>6</sup>Li MAS NMR where **Figure 1** demonstrates the spectrum obtained at 268 K. One-dimensional SI measurements of Li<sup>+</sup> exchange were found to be more efficient and more accurate than 2D EXSY for this material.<sup>7</sup> In the SI experiments a single <sup>6</sup>Li resonance is selectively inverted using a soft Gaussian shaped pulse to excite a narrow frequency range, following which the system is allowed to return to equilibrium over a series of mixing times before detection of the magnetization.<sup>8</sup> Analysis revealed moderately fast rates for all three exchange pairs as well as low energy barriers for all Li ion hopping processes which correspond well to the known Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> structure.

Recently sulphate based materials, in particular the LiMSO<sub>4</sub>F (M=Fe, Mn, Mg) class of materials, have

shown promise due to the favourable electrochemical properties associated with these structures including a high redox potential consistent with the increased electronegativity of the sulphur atom as compared to phosphorus.<sup>9</sup> As such, <sup>6,7</sup>Li and <sup>19</sup>F solid-state NMR are being used to characterize local environments within these phases and <sup>6,7</sup>Li{<sup>19</sup>F} REDOR experiments can be implemented to observe Li ion mobility across a range of temperatures. The results can then be used to compare ion dynamics in these materials to related polyanion structures.



**Figure 1:** <sup>6</sup>Li solid-state NMR spectrum of Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> at 268 K depicting three Li resonances corresponding to three unique crystallographic Li sites

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