

Li and V MAS NMR Studies of the Electrochemical Behavior of $\text{Li}_{1+x}\text{V}_3\text{O}_8$

Nicolas Dupré^a, Joël Gaubicher^b,
Dominique Guyomard^b, Clare P. Grey^a

^aDepartment of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794, USA

^bInstitut des Matériaux Jean Rouxel, Laboratoire de Chimie des Solides, BP 32229 44322, Nantes Cedex 3, France

Recent developments in portable technology have created a high demand for batteries with high energy densities and long cycle lives. A great deal of interest has been focused on a wide variety of lithium intercalation compounds as possible cathodes in rechargeable batteries. Here we report both NMR and diffraction studies of a series of vanadium-containing intercalation compounds.

Structural properties are strongly related to the electrochemical performance of cathode materials for Li rechargeable batteries. The information obtained from XRD data is limited to long-range structural order and not sensitive to light elements such as lithium. Therefore, XRD is unsuitable for probing local structure in disordered materials. Recently, ^6Li and ^7Li MAS NMR spectroscopy have been applied to examine the variations in local structure of cathode materials for Li rechargeable batteries.

$\text{Li}_{1+x}\text{V}_3\text{O}_8$ has a layered framework suitable for reversible lithium intercalation processes and can allow 4 lithium ions per unit formula to be inserted. Moreover, the compound forms a continuous solid solution during cycling, in contrast to $\text{V}_2\text{O}_5\text{-}\alpha$ where a 2 phases transition occurs. Benedek et al. [1], Thackeray et al. [2] and Jouanneau et al. [3] have performed DFT calculations in order to determine the cation sites that are occupied at the different stages of the lithium intercalation but no insertion mechanism has been proposed.

^7Li and ^{51}V MAS NMR spectra acquired during the electrochemical cycling of the layered materials $\text{Li}_{1.2}\text{V}_3\text{O}_8$ will be presented. These two NMR probes have been used to follow the local rearrangements around the different lithium and vanadium sites during the different stages of the intercalation/deintercalation process. Three different resonances are observed using ^{51}V MAS NMR in accordance with the structure and have been assigned to the three vanadium sites on the basis of their different symmetries and different sidebands manifolds. Good resolution can be obtained only for the reduced samples suggesting a metallic behavior and delocalized electrons. Moreover, the progressive shift of the isotropic resonances observed between 4.2 and 3.0 V using both Li and ^{51}V MAS NMR confirms the electrochemical solid solution behavior

A wide variety of vanadium-containing materials were investigated to develop a fundamental understanding of some of the electronic phenomena that control the NMR shifts typically observed in these compounds. These phenomena may come from the presence of PO_4 groups, the level of distortion of the vanadium octahedra and/or the angles of the V-O-V bonds.

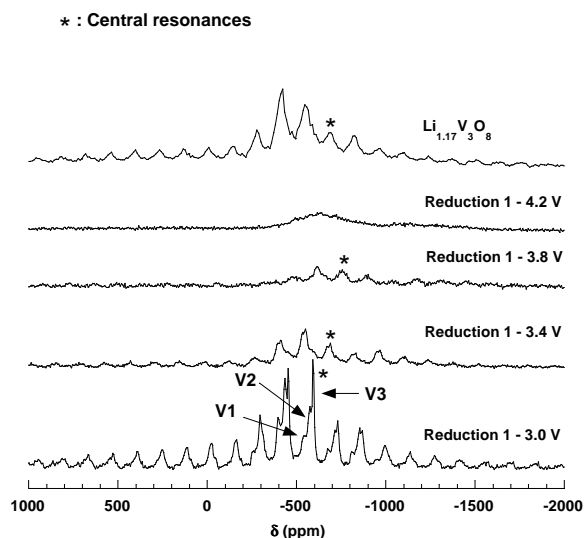


Figure 1. Quantitative ^{51}V MAS NMR spectra of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ acquired at $B_0 = 7.1$ T ($\nu_r = 13$ kHz)

References

1. Benedek R., Thackeray M.M., Yang L.H., Phys. Rev. B, 60-9, 6335 (1999).
2. L.A. de Picciotto, K.T Adendorff, D.C. Iles and M.M. Thackeray, Solid State Ionics, 62 (1993) 297
3. Jouanneau S., These IMN, Laboratoire de Chimie des Solides, Nantes (2001)