Revealing Li^+ Exchange in the β-modification of Li_3VF_6 by ^{6}Li 2D MAS NMR Spectroscopy

P. Bottke,[1] S. Nakhal,[2] M. Lerch,[2] P. Heitjans,[1] M. Wilkening[1]

[1]Leibniz Universität Hannover, Institut für Physikalische Chemie, Callinstr. 3,
D-30167 Hannover, Germany, E-Mail: bottke@pci.uni-hannover.de

[2]Technische Universität Berlin, Institut für Chemie, Str. des 17. Juni 135,
D-10623 Berlin, Germany

1 Introduction

The site-specific characterization of Li^+ jump processes in solids increasingly gains in importance in lithium-ion battery research. In the present study, high-resolution ^{6}Li and ^{7}Li 2D NMR,[1–4] carried out at ultra-fast magic angle spinning (MAS), is used to reveal Li^+ exchange in the model compound β-Li_3VF_6. The results are compared with those of the α-form of Li_3VF_6, which has been investigated quite recently.[5] The two modifications are characterized by a different number of magnetically inequivalent Li sites leading to well-resolved ^{6}Li and ^{7}Li NMR spectra. The Li ions in α-Li_3VF_6 (space group *Pna*2$_1$) reside in three distinct octahedral sites forming a chain by face-sharing. This is in contrast to the much more complex situation in the β-modification (*C*2/*c*) where the Li ions are distributed among one tetrahedral and four octahedral voids. These Li(*i*) sites ($i = 1 \ldots 5$) are manifoldly connected to each other by face-, edge- and corner-sharing. The combination of results from temperature-variable exchange NMR with structural information allowed the identification of those sites preferentially involved in Li diffusion and, thus, the determination of the most probable migration pathways.

2 Results

As an example, in Fig. 1 a typical ^{6}Li 2D exchange NMR spectrum of β-Li_3VF_6 is shown. The spectrum has been recorded with a NOESY pulse sequence at 88 MHz and a mixing time of $t_m = 40$ ms. Off-diagonal intensities reveal slow Li^+ exchange processes between the five crystallographically distinct sites in β-Li_3VF_6. Obviously, hopping between A and B as well as between A and E is preferred to other exchange processes, *e. g.*, B ↔ C and C ↔ D, showing up in the 2D contour plot. This is corroborated by additional ^{6}Li 2D MAS NMR spectra recorded at shorter t_m. The assignment of the five NMR lines shown in Fig. 1, being to our opinion the most probable one, is based on both structural information and the relevant electron spin density transfer mechanisms.[4] In the present case, mainly positive spin density is transferred from the vanadium centers (electron configuration $t_{2g}^2 e_g^0$) to the Li cations either directly or via the delocalization mechanism involving the p-orbitals of the fluorine anions. The latter mechanism requires an Li-F-V angle of 90° for optimal overlap.[1-5] Most likely, the exchange process A ↔ B reflects Li exchange between the sites Li(3) and Li(4); the corresponding LiF_6-octahedra are connected by face-sharing. In agreement with temperature-variable ^{6}Li 1D MAS NMR spectra, the β-phase reveals a much slower Li exchange than observed for the α-form.

The three NMR lines of the latter clearly coalesce at elevated temperatures.[5] This is in contrast to the β-modification of Li_3VF_6 where no coalescence of the five distinct NMR lines, ranging from 30 to 75 ppm, is observed.

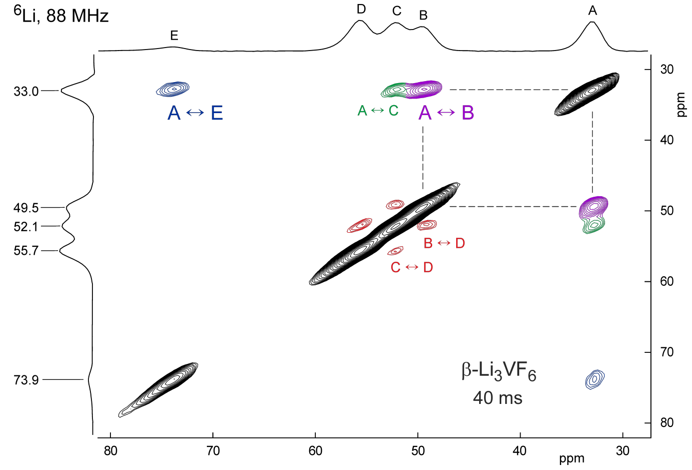

Fig. 1: ^{6}Li 2D MAS NMR spectrum of polycrystalline β-Li_3VF_6 measured at $T = 338$ K (bearing gas temperature) and a spinning speed of 60 kHz. Data have been recorded using an Avance III spectrometer (Bruker) at a resonance frequency of approximately 88 MHz corresponding to an external magnetic field of 14.1 T. The spectrum has been acquired at $t_m = 40$ ms.

3 Conclusion

Exchange NMR, which takes advantage of hyperfine shifts, is a highly versatile tool to elucidate Li jump processes in paramagnetic compounds being of interest as cathodes in lithium ion batteries. By using both structural data and information from interactions of the transition metal d-electrons and the Li nuclei, the site-specific NMR hyperfine shifts can be understood. The appearance of cross-peaks in 2D exchange NMR spectra provides valuable insights into the Li ion dynamics. This might help to determine the structural details mainly affecting lithium transport.

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