

Solid-State NMR Study of Alkali Ion Dynamics in Layered $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Li}_2\text{Ti}_3\text{O}_7$

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In $\text{Na}_2\text{Ti}_3\text{O}_7$ having monoclinic layer structure the sodium can be replaced completely with lithium to achieve monoclinic $\text{Li}_2\text{Ti}_3\text{O}_7$ [1, 2]. Both materials exhibit interesting properties such as zero-strain behavior upon intercalation and high cycling stability in case of potential battery application. However, there is still a lack of fundamental understanding of the ion diffusivity of both Na and Li in the corresponding host structure. Solid-state nuclear magnetic resonance (NMR) spectroscopy is used here to study the dynamics of both alkali ions in layered $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Li}_2\text{Ti}_3\text{O}_7$. This includes activation energies for the ionic motion and jump rates on the microscopic scale from ^{23}Na and ^7Li NMR spin-lattice relaxation (SLR), ^7Li spin-alignment echo (SAE), and 2D ^6Li NMR exchange techniques. Moreover, the dimensionality of the ionic motion is investigated by frequency-dependent ^7Li NMR SLR. Structural details are studied using magic-angle spinning (MAS) ^{23}Na and ^7Li NMR spectroscopy. Results for the electric field gradient at the Na and Li site, respectively, are compared with those from theoretical calculations performed within this study. The dynamics are similar for both cations, and the frequency-dependence of the ^7Li NMR SLR rate indicates Li motion confined to two dimensions. Thus, these two materials may be regarded a model system for low-dimensional diffusion [2]. Another system studied by us also offering low-dimensional diffusion pathways both for Li and Na ions is mixed-alkali $\text{Li}_x\text{Na}_{2-x}\text{Ti}_6\text{O}_{13}$ [3].

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