Extremely slow Li exchange processes in diamagnetic Li_2ZrO_3 followed by ^{6}Li 2D EXSY NMR

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Two-dimensional (2D) ^{6}Li exchange magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy, see, *e.g.*, Refs. [1-5], was used to probe extremely slow lithium hopping processes in a polycrystalline powder sample of lithium zirconate, Li_2ZrO_3. In agreement with the crystal structure of Li_2ZrO_3, the ^{6}Li MAS NMR spectra, recorded at MAS frequencies of up to 60 kHz, are composed of two signals showing up at – 0.10 ppm and 0.26 ppm (referenced to 1 M $LiCl_{aq}$). The two signals are of equal intensity and reflect the two magnetically (and electrically) inequivalent Li sites in the zirconate. While 1D MAS NMR spectra were recorded after an excitation with a single $\pi/2$ pulse, a three-pulse sequence was used to carry out 2D exchange spectroscopy (EXSY) NMR measurements at an MAS frequency of 12 kHz. Due to the slow Li diffusivity expected, in some cases the measurement time reached seven days to acquire a single 2D NMR spectrum. At sufficiently long mixing times of up to 1 min, the contour plots clearly reveal off-diagonal intensities indicating an extremely slow two-site exchange process with rates as low as 60 jumps / hour. This corresponds to a self-diffusion coefficient in the order of 10^{-22} m^2 s^{-1}. To our knowledge, this is, so far, one of the slowest Li solid-state diffusion processes probed by ^{6}Li 2D exchange MAS NMR.

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