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Diffusion in $Li_xNa_{2-x}Ti_6O_{13}$ investigated with impedance spectroscopy

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Within the system Li_2O – TiO_2, lithium hexatitanate $Li_2Ti_6O_{13}$ (*i.e.* $Li_2O \cdot 6\ TiO_2$) was already studied before by electrochemical methods with respect to its application as a potential Li-ion battery anode material [1, 2]. This compound is also attractive for fundamental cation diffusion studies, in particular due to its channel structure and the fact that Li and Na are interchangeable. The present work examines the effect of different Li : Na ratios in $Li_xNa_{2-x}Ti_6O_{13}$ on diffusion using impedance spectroscopy which measures the conductivity over a wide frequency range and thus on different length scales. This also enables the comparison with NMR results obtained by us in a separate study. Additionally, the Hebb-Wagner polarization (DC polarization) method is being used here to discriminate between the cation and a partial electronic conductivity [3].

$Li_xNa_{2-x}Ti_6O_{13}$ with $x = 0$, 0.33, 1 and 2 has been prepared via solid-state synthesis starting from $NaCO_3$ and TiO_2 to obtain phase pure $Na_2Ti_6O_{13}$. To remove sodium from the structure, an ion-exchange reaction using molten $LiNO_3$ is used [1, 2]. Depending on the reaction time, different Li : Na ratios are achieved up to the fully exchanged $Li_2Ti_6O_{13}$. Structure and phase confirmation is obtained via X-ray powder diffraction (XRPD) and inductively coupled plasma optical emission spectroscopy (ICP-OES). $Na_2Ti_6O_{13}$ (space group C2/*m*) is a channel-structured material with two Na positions per unit cell supposed to be solely located within a channel. The lattice parameters vary little during substitution of Na with Li, only leading to a change from an eight-fold (Na ion) to a four-fold (Li ion) position within a cubic cell of eight oxygen atoms [2].

The impedance data of $Li_xNa_{2-x}Ti_6O_{13}$ for the different compositions x and temperatures in the range $T = 253\ldots413$ K are analyzed in various basically equivalent representations (*e.g.* [4]). AC impedance plots $-Z''(\omega)$ vs $Z'(\omega)$ show essentially single semicircular arc behavior. However, the complex modulus representation $M(\omega) = M' + iM''$ reveals a somewhat more involved electrical response. Depending on the Li : Na ratio, the $M''(\omega)$ spectra show a single peak for $Na_2Ti_6O_{13}$ and a continuous change to two peaks for $Li_2Ti_6O_{13}$. Plotting the real part of the conductivity σ' vs. $\omega/2\pi$ (10^{-1} to 10^7 Hz) yields in each case a plateau in the low frequency region (10^{-1} Hz to 10^2 Hz) representing the dc conductivity. It shows Arrhenius behavior with activation energies of 0.8 to 0.9 eV, roughly independent of x. An influence by an electronic contribution to conductivity seems unlikely due to the insulating properties (band gap $\geq$ 3eV [5, 6]). This can be shown by DC polarization measurements being presently performed in our laboratory in the same temperature range as the impedance spectroscopy measurements. First results confirm that $Li_xNa_{2-x}Ti_6O_{13}$, besides being a mixed cationic, is a mixed mainly ionic conductor with only a small electronic contribution.

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