Topological Constraints of Lithium Diffusion in Oxide Glasses

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This study focuses on investigating characteristics of lithium mobility in different types of oxide glass networks, by means of impedance spectroscopy (IS), fs UV inductively coupled plasma mass spectrometry (ICP-MS) and Raman spectroscopy. The aim is on understanding what is the dominant mechanism behind Li-diffusion, how is it influenced by composition, various degree of structural order and the isotope effect. Systems of choice are oxide glasses where network is formed by Si, Si–Al, B or P structural units with Li as the only mobile species. For purposes of comparison, glass compositions were selected for stability at ambient conditions and with a comparable Li-content, *i.e.*, similar Li : T ratio, where T = Si + Al + B + P.

IS results show the highest activation energies in the Li-borate glass group ($0.25\,Li_2O \cdot 0.75\,B_2O_3$ sample, $E_a = 85.2 \pm 1.0$ kJ $\cdot$ mol^{-1}) while the lowest was observed for aluminosilicates with Li : Al = 1, *i.e.*, $LiAlSiO_4$ (eucryptite) and $LiAlSi_2O_6$ (spodumene) compositions with 67.5 ± 0.9 and 68.9 ± 0.4 kJ $\cdot$ mol^{-1}, respectively. The concentration of available mobile Li-particles does not seem to play a decisive role, as *e.g.*, $LiAlSi_2O_6$ has about half amount of Li compared to $0.25\,Li_2O \cdot 0.75\,B_2O_3$ glass. Li-borate glasses were also the most ineffective for long-range transport of lithium, probed by isotope exchange experiments with subsequent profiling with ICP-MS. Self-diffusion coefficient at 476 K is $\log D = -15.75$ for $0.25\,Li_2O \cdot 0.75\,B_2O_3$ but $\log D = -13.20$ for $LiAlSiO_6$ (with D in m$^2 \cdot$ s^{-1}). Li-silicates with the higher Li-content (> 20 mol% Li_2O), are comparable in Li mobility to spodumene glass, but are notably more structurally constrained, which can be expressed through the HR/f ratio given by the ratio of diffusion coefficients measured by isotope exchange experiments and derived from electrical conductivity measurements. For Li-trisilicate ($Li_2Si_3O_7$) the correlation factor is ca. 0.5 which points toward only about 50 % of all jumps being successful for long-range transport. For spodumene glass, as well as for $0.2\,Li_2O \cdot 0.8\,P_2O_5$ the correlation factor is close to 1, an indication of uncorrelated motion of lithium atoms.

In summary, it can be concluded that different oxide networks result in different local potential landscape but similar E_a. Potential landscape, or more precisely the spatial distribution of suitable low potential sites appears to be the dominant control for Li-mobility. In that respect polymerized aluminosilicate networks (with Li : Al = 1) are the most supportive structures while binary Li-borate networks are the most impeding for Li-mobility within the studied systems. Overall, structure, contrary to Li-concentration, is the predominant defining factor in qualifying oxide glass types as high-performing solid electrolyte candidates.