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Kinetics of Lithium Intercalation in Chalcogenide Single Crystals

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Intercalation and deintercalation of lithium in electrodes are the fundamental chemical reactions in lithium batteries. A systematic study of Li diffusion in single crystal layered-dichalcogenides with different lattice parameters has been performed under ambient and elevated pressure. Single crystals of TiS_2, $TiSe_2$, $TiTe_2$, and TaS_2, were prepared by chemical vapor transport and subsequently intercalated using n-butyllithium (BuLi) solutions in hexane [1–3]. Diffusion of lithium was mainly studied parallel to the *ab* plane of the single crystals. The preparation technique has been refined significantly in order to avoid alteration of the crystals during the experiment and to avoid any diffusive contributions along the crystallographic *c*-axis direction [3]. Analyses of profiles have been carried out initially by UV-femto-second laser ablation ICP-OES. However, this technique is applicable only to very long profiles since large rates of ablation are required for the detection, resulting in significant damage of the crystals. The analytical techniques could be improved using high sensitivity inductively coupled plasma mass spectrometry (ICP-MS), requiring two orders in magnitude lower amount of material for the detection. Important findings were (i) diffusion of Li is similar in TiS_2 and TaS_2 despite of different lattice parameters and electronic properties of the materials and (ii) pressures up to 500 MPa have only minor effect on Li diffusion in TiS_2 and $TiSe_2$ but strongly decrease diffusion in $TiTe_2$.

Additional experiments have been carried out to define the diffusivity in the *c*-axis direction. For analysis of the short profiles secondary ion mass spectrometry (SIMS) was applied, and a new protocol was developed for LA-ICP-MS allowing the measurement of diffusion profiles as short as 3 µm in depth [4]. For different chalcogenides it was established that diffusion is slower by more than 3 orders of magnitude in *c*-direction than within the *ab* plane.

Isotope exchange experiments with pre-intercalated crystals of TiS_2 were used to determine the controlling step during chemical intercalation with BuLi. The results imply that after the absorption of BuLi at the crystal surface, butyl radicals can freely jump from one to the next lithium atom. The jump sequence is finalized by either desorption of BuLi molecules or formation of octane by two adjacent butyl radicals, an irreversible step [2]. Sorption and desorption of butyl lithium on the crystal surface and hopping of butyl radical between surface sites are fast compared to deactivation of butyl radicals and intracrystalline diffusion of Li.

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