

Thin Film Intercalation Compounds: UHV Deposition
and Changes of Electronic Structure
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electrochemical potentials in very detail. It is expected that such investigations will allow to get a better insight into the thermodynamics of intercalation but also into the mechanism of concurrent reactions which may lead to the capacity loss of batteries with cycling.

The preparation and investigation of thin film intercalation materials is of interest for two reasons: from a fundamental point of view many interesting properties as e. g. the electronic properties can well be studied using thin film materials. From an application point of view solid state microbatteries for integration are of growing interest.

We have prepared thin films of TiS_2 and V_2O_5 by MOMBE and PVD in UHV preparation chambers, which are coupled to surface science systems allowing their characterisation with photoelectron spectroscopy of the core level and valence band region. The intercalation reaction can be either performed by deposition of guest species e. g. alkali onto the substrate surfaces. Also working battery devices can be prepared and characterized in UHV which allows the combined investigation by electrochemical and spectroscopic techniques. Thus changes due to intercalation, the stability range, and possibly formed decomposition products can be easily followed. In addition, information on the intercalation induced changes in electronic structure, of the changes of electrochemical potentials given as shifts of the Fermi level, and relative atomic redistribution of electronic charge due to intercalation can be investigated.

TiS_2 shows a reversible intercalation of Na up to a stoichiometry of about 1. The intercalation reaction cannot be described in terms of the rigid band model as an energy gap opens between the S3p and Ti 3d levels with intercalation. This is in contrast to Na intercalation into TiSe_2 . From the relative shifts of core level lines and changes in work function the change in charging due to charge transfer are deduced and the results show that additional electronic charge from the Na is transferred to Ti but also to S. The comparison of Fermi level shifts equivalent to changes in electrochemical potentials of electrons to the changes of battery voltage with Na stoichiometry indicates that about 60% of the driving force of intercalation is due to electron transfer.

The intercalation of Na and Li in V_2O_5 thin films proceeds without evident decomposition up to a stoichiometry of about 1. The charge transfer with intercalation leads mostly to a change of the V oxidation state which is evidently due to the more localized electronic structure of the oxides compared to the sulfides. The valence band shows the occupation of originally empty V 3d states which, however, are situated below the Fermi level with a gap of approximately 0.5 eV. This effect is attributed to the formation of a polaron state due to an electron driven distortion of crystal structure. The changes in work function can be again correlated to the changes in intercalation battery voltage.

In summary, the investigation of thin film devices of intercalation materials allow to characterise the changes in electronic structure and related properties of