## Reversible electrochemical reactions of metal fluorides with Li

## H. Li and J. Maier Max-Planck-Institut für Festkö rperforschung D-70569 Stuttgart, Germany

Recently we have systematically investigated the electrochemical reactions between  $MF_n$  (M = Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ag, Sn, Ca, Ba; n=1-3) and Li in a Li/MF<sub>n</sub> cell at a wide voltage range (0-4.3 V).

During the first discharge, most of metal fluorides can be decomposed after *n* molar Li is inserted, except  $CaF_2$ and  $BaF_2$ , which have relatively higher formation energy and hence very low decomposition voltage (emf < 0.09 V). They cannot be decomposed before the deposition of metal Li (-20 mV) due to a marked overpotential. During the charge process, a certain amount of Li can be extracted out from M/LiF nanocomposites in the cases of M=Ti, V, Mn, Fe, Co, Ni and Cu. The electrochemical Liinsertion/ extraction reactions for these fluorides can be written as:

$MF_x + xLi^+ + xe^- \rightarrow M/LiF$	(1)
$M/LiF - xLi^+ - xe^- \rightarrow MF_x$	(2)

This reaction mechanism has been confirmed in the cases of  $TiF_3$  and  $VF_3$  based on the results of XRD and Raman spectroscopy. HRTEM observation on  $TiF_3$  indicates that a full Li-insertion transforms metal fluorides into an amorphous composite of M/LiF. Upon full charging, the original phase is restored partially and the grain size of reformed  $TiF_3$  is about 10 nm. Some amorphous regions are still remaining corresponding to a capacity loss during the first cycle.<sup>1</sup>

In order to understand the influence of the microstructure on the electrochemical performance, we prepared a series of Ti/LiF composites by mechanical milling. The particle size of Ti and LiF precursors was reduced with increasing milling time and Ti and LiF were dispersed on a submicrometer scale. It was found that the amount of extractable Li was larger in a composite milled for a longer time, but still far less than that from a Ti/LiF composite formed *in situ* via reaction (1).

The above results indicate that the reason for chemical very stable LiF showing a high reactivity in reaction (2) is due to an atomic-level dispersion with transition metal. Such a microstructure is certainly kinetically very favourable. A similar phenomenon had also been observed in the cases of transition metal oxides by Tarascon's group.<sup>2</sup>

Among all metal fluorides studied, TiF<sub>3</sub> and VF<sub>3</sub> show better reversibility for reaction (2) and higher Li-storage capacity of 500-600 mAh/g (Fig.1). In view of thermodynamics, both exhibit higher formation energy and hence a relatively low voltage for the reaction (2) (1.4 V and 1.9 V respectively). On the other hand, they may also have some kinetically advantages, which need further clarification. While in the case of SnF<sub>2</sub> where Sn can alloy with Li in a low voltage range (<0.8 V), the reaction (2) was not investigated in the same voltage range of 0-4.3 V. However, when the cycling of the battery limited between 0.9 V and 4.3 V and the alloy reactions avoided completely, it was observed clearly that small amounts of is obviously less than the capacity in the sloped region during discharge. It means that extra Listorage occurs within the sloped region during discharge. ESR results showed that the chemical state of Li in the sample within the sloped region seems to be approaching the nature of Li upon insertion of Li ion. HRTEM did not show significant growth and decomposition of the SEI film within the sloped region. Therefore we suggest here that the extra Li-storage in the sloped region is mainly caused by an interfacial charging of the M/LiX matrix (it seems that half of the extra Li-storage is related to this in M/Li<sub>2</sub>O systems<sup>3</sup>), instead of the formation/ decomposition of a polymer-like solid/electrolyte interphase (SEI) film on electrode surface, which seems to be more significantly observed in the cases of transition metal oxides.<sup>2</sup> The Li-storage by interfacial charging may be a new concept for electrochemical supercapacitor application.

It should be mentioned here that transition metal fluorides can also show rather high rate performance (i.g. VF<sub>3</sub> and TiF<sub>3</sub>, 1.5 C, ~60 % capacity retention), although the raw materials are poor electronic conductors and have a particle size on a micrometer scale. This is related to the formation of nanoscale microstructure after Li-insertion, leading to improved kinetic properties.

In brief, our studies confirm the general possibility of reversible storing Li heterogeneously via phase formation even for the chemically very stable fluorides, when both thermodynamic and kinetic acquirements are satisfied, especially when the size of a reaction system is on a nanometer scale, showing reduced transport pathways, special interface chemistry and/or size effects on these properties.<sup>4</sup>





Li could be extracted reversibly. It indicates that Li-M alloying/de-alloying reactions are not favourable for reaction (2).

For all metal fluorides of which the parent metal cannot alloy with Li, it was noticed that extra Li with a capacity of 200~400 mAh/g is stored within M/LiF nanocomposite, showing a sloped feature at low voltage in the voltage profiles. The capacity in the sloped region during charge References:

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