1 Introduction

The intercalation reaction has fascinated researchers of several areas over the past 40 years. It involves two species, one playing the role of the host, the other of the guest. Typically host and guest interact weakly, and they give place to a compound where they can still be considered two distinct entities. In many cases, the amount of guest species in a host can be arbitrarily varied, so that the perturbation to the environment of both host and guest can be controlled in a defined manner. Structural changes correspond to changes of the physical properties, thus for both entities and for the resulting complex it is often possible to tailor a desired behavior. The properties of the intercalated materials can be finely tuned because the host can be often prepared in a wide range of compositions by intermixing of different related elements.

Transition metal dichalcogenides (TMDCs) form a class of compounds known for their layered structure, where the term “layered” refers to the existence of parallel planes, where bonds are much weaker than inside the region that they limit. Such feature makes these materials highly anisotropic and in extreme cases two-dimensional. A large variety of properties arise from this peculiarity, rendering TMDCs interesting not only from the theoretical point of view (e.g. charge density waves [1-4], superconductivity [5-7]), but also for various practical applications. Due to their low shear resistance TMDCs are used as solid-state lubricants [8-13]. TMDCs can readily exhibit saturated, chemically inert surfaces, which are an ideal substrate for surface science studies. They have a high absorption coefficient ($10^5$ cm$^{-1}$ [14-16]) and some of them are semiconductors with a direct band gap of 1.3-2.0 eV, perfectly matching the solar spectrum. Tributsch and coworkers demonstrated in 1977 that highly efficient and relatively stable photoelectrochemical cells can be based on TMDCs [17, 18]. Due to the reactivity of the plane edges TMDCs proved to be very efficient in heterogeneous catalysis. MoS$_2$ hydrodesulfurization catalysis is one of the most widely used catalytic systems worldwide [19].

A layered structure is also the only one which in a literal sense can be intercalated. This linguistic ideality is also physical because layered materials represent the most suitable host for intercalation. The intercalation of alkali metals in graphite was discovered in 1926 [20]. Very early studies concentrated on the intercalating ability of TMDCs with alkali metals [21, 22]. In the year seventies it was realized that this reaction was responsible of the reversible behavior of some TMDC/Li batteries [23, 24]. This finding initiated intensive efforts to produce a new generation of devices with mass-production potential. In the 80ies it was demonstrated that by using oxides instead of chalcogenides working devices with higher performance were possible, and the mainstream of battery research abandoned TMDCs. Since the mass production started by Sony in
1991 intercalation batteries proved their high competitiveness in the market of rechargeable power supplies becoming in 1997 the first portable cell as sales [25]. Today the intercalation battery is rather a problem of industrial process more than of materials even if many fundamental problems of intercalation still remain unclear.

Nevertheless, the discovery that metal intercalation can be obtained in ultra-high vacuum (UHV) by deposition of the guest on top host of the started new interest on TMDC intercalation [26, 27]. In fact it is possible to study in UHV with surface science techniques (photoelectron spectroscopy, first of all) the chemical, structural and electronic effects of intercalation. Since the beginning of this approach, again several research groups reported an exhaustive amount of investigations (see Chapter 2).

Since 1969 several review articles and books have described the properties of TMDCs [14, 28, 29] and their intercalation complexes [30-36].

Thus, the question may arise, how a Ph.D. thesis on the alkali intercalation of TMDCs investigated by means of photoelectron spectroscopy can today still push the limits of knowledge.

In the last two decades the significant improvements of scientific equipment for the investigation of solid structures has brought about decisive factors to the understanding and development of new materials. Thanks to several diffraction techniques the atomic arrangements in intercalation compounds are known with great accuracy for each investigated system. However, in spite of the importance of intercalation for energy storage a detailed and quantitative understanding of the energetics of this reaction is still far from being accomplished. No general agreement has been reached on the charge redistribution after intercalation, or on the role and nature of the interactions between host, guest and itinerant electrons. These aspects are of crucial importance for an understanding of the mechanism of energy storage. Indeed, this comprehension would be of valuable support to the estimation of the theoretical performance of a possible electrode material before preparing and testing it. Both crystal and electronic structures are affected by intercalation, but the latter can give a more quantitative picture of mutual interactions.

By means of photoelectron spectroscopy the electronic structure is directly accessible. However, UHV investigations were always limited to model experiments that could not satisfactorily reproduce the control one has on the formation of the intercalated compound if operating in an electrochemical cell. In particular high guest concentrations proved to be not attainable, and any issues on the reaction reversibility could not be addressed. This work was intended to make some steps into this direction. The limiting guest concentration in previous work on UHV intercalation was explained as due to fast ionic diffusion into the bulk of the crystals that are typically used as substrate [37]. To overcome this effect one can think to use hosts of minimal
thickness on not intercalating substrates. The guest will be then confined within a small depth and its concentration rapidly increased with small amounts of the deposit. Therefore, in this work the host was prepared in the form of thin films in the same UHV system where the intercalation was subsequently investigated by means of photoelectron spectroscopy (PES). This prevents the adsorption of interfering species (as it is the case after contact with air), and assures a surface quality comparable to that of *in-situ* cleaved crystals.

Additionally, thin films prepared with the same procedure were integrated in solid-state electrochemical cell, which could be operated in UHV in a coupled electrochemical and PES measurement. Thus, not only the guest concentration can be controlled as never reached before. Since the electrode potential depends on the free energy of intercalation, a correlation between thermodynamic and electronic structure is also possible. This technique should provide an experimental fundament to the selection and design of electrode materials.