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Surface science studies of the diffusion of adsorbed and intercalated lithium

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ABSTRACT

Due to its small size and high ionization affinity, lithium exhibits excellent diffusion properties making it a proper candidate for intercalation ion batteries. We briefly review the experimental surface science studies on the diffusion of Li on solid surfaces, including our own work, and the first nm-scale studies of Li intercalation. Particular emphasis has been placed on the presentation of the surface science approach including the thorough preparation of the substrate surface in UHV, the control of the surface structure and chemical composition before and during the experiments, and the critical quantitative consideration of external factors such as temperature, electric or magnetic field, or the presence of reactive gases. Using Li as an exemplary case, typical methods and experimental procedures employed in surface diffusion studies are presented, that may eventually lead to a better understanding and further improvements of the transport properties of adsorbed and intercalated Li.

1. Introduction

Lithium-ion batteries provide an effective and compact energy storage technology suitable for almost all portable and stationary applications. Their energy density and thus effectivity essentially depend on the specific Li storage capacity of the constituent electrodes [1,2]. Among the many processes involved in the build-up of Li-storage and its discharge, Li diffusion plays an important, but sometimes underestimated, role. Particularly, the negative electrode should be able to concentrate Li during the lithiation process via insertion or intercalation; for both processes the diffusion of Li plays a critical role. The lithiation behavior of the electrodes has been found to be not only material-specific, but also certain crystallographic directions are preferred Li insertion routes [3]. Once more, this property is well known from Li diffusion studies [4].

Since the 1990s, an increased focus is directed on “all-solid-state Li-batteries” in which liquid electrolytes are substituted by non-flammable solids [5]. If technologically realised, such alternatives would significantly improve safety and enable using electrodes with higher energy density, e.g. using Li metal as the anode [5,6]. However, despite recent breakthroughs which have led to a significant increase in lithium-ion conductivity, further search for new materials is necessary, in order to achieve a stable Li conductivity that is close to that of liquid electrolytes, i.e. 10^{-1}–10^{-3} S cm^{-1} at room temperature. Apart from developing new complex materials, the fundamental understanding of conductivity mechanisms is crucially important for the development of novel Li-ion batteries.

Considering the physical parameters that are determining the ionic conductivities of crystalline solids, such as solid-state inorganic lithium conductors, there is an apparent correlation between the lithium-ion conductivity and the diffusional properties of Li [7]. Particularly, the surface and interlayer diffusion of Li and field-effects on Li migration on solid surfaces are relevant for lithium-ion conductivity research.

The description of Li diffusion “in” and “on” solid anode materials is manifold and comprehensive. However, apart from a few exceptions (as e.g. [8]), most studies are performed in a way which differs from the classical surface science approach. In classical surface science, great attention is paid to control the substrate cleanliness and the oxidation state of the diffusing adsorbate (in the present case Li), as well as the adsorbate coverage (see e.g. review [4] and references therein). The latter is particularly important in the case of Li, where strong repulsive dipole-dipol interaction significantly influences the strength of the adsorption bond and thus the activation energy of diffusion [9]. Many measurements have been performed under electrochemical conditions in the presence of electrical fields, the exact strength of which has often been unknown. Again, this is particularly important for Li, since the high ionicity of alkali adsorbates leads to a high sensitivity of diffusivity on the electric field [10–12]. The mentioned factors explain the wide range of the reported diffusion data (e.g. an extremely wide range is reported for Li diffusion coefficients along the graphite basal plane: D $\sim 10^{-6}$ to 10^{-10} cm^{2}s^{-1})

In theoretical studies, Li transport within Li-ion batteries is often analyzed using considerations based on the macro-homogeneous porous electrode model, originally developed by Newman et al. [13]. It

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assumes that the process of lithium insertion always obeys the Fick's laws, an assumption which not always holds true, particularly at high Li coverages when Li—Li interactions remarkably influence the diffusion process.

The aim of this short review is to provide a "surface science view" on Li-diffusion, in order to highlight the importance of carefully controlling the surface purity and the Li coverage/oxidation state as well as to consider such important parameters as crystallographic orientation, local structure, defect density, and crystallite size of the substrate.

2. Lithium on solid surfaces

The small size of Li adatoms and the strong ionic component in their adsorption bonds leads to a high sensitivity of Li to the electronic structure and potential relief of the substrate. This has stimulated attempts to use adsorbed Li adatoms as "probes" that reveal peculiarities of alkali interactions on solid surfaces. This idea turned out to be very effective for metal surfaces: e.g. LEED experiments of lithium adsorption on atomically rough W(112) [14] and Mo(112) [15] surfaces allowed to discover the long-ranging indirect adatom-adatom interaction, mediated by the electronic system of the substrate, decades before such an interaction was observed for Ce atoms on Ag(111) by STM [16]. In turn, by studying Li adlayers on Re$(\bar{1}010)$ – and Re$(10\bar{1}0)$ – surfaces, which differ solely by fine atomic structure details due to the second layer, the relative contributions of different types of adatom interaction were evaluated [17]. Generally, Li adlayers represent a prime example of model systems for a rich variety of superstructures, 2D-phase transitions and ordering and disordering phenomena [18].

The same "size and bonding" reasons turn Li into an effective probe to study the specifics of diffusion on solid surfaces, since Li adatoms are extremely sensitive to the geometric and electronic anisotropy of the substrate surface, both of which are essential factors in surface diffusion. The remarkable dipole moments of Li adatoms provide also a high sensitivity of Li to an applied electric field, i.e. making Li an excellent probe for studying field-induced and field-stimulated diffusion and electro-migration.

3. Surface diffusion of lithium

3.1. Experimental methods

The most straightforward method to study surface diffusion of adatoms is to follow the thermally activated motion of individual atoms and evaluating the surface diffusion coefficient as.

$$D = \langle \Delta x^2 \rangle / 2\tau, \tag{1}$$

where $\langle \Delta x^2 \rangle$ is the mean square displacement and τ the corresponding motion time. Such observations can be made only when single adatoms are placed on an empty surface or when the adatom density is extremely low. Using a field ion microscope (FIM), which images the surface of an apex of a nanosized tip-shaped sample with atomic resolution by field ionized noble gas atoms [19,20], the motion of individual atoms can be monitored and the diffusion coefficient can be extracted using Eq. (1). Starting with the pioneering work of Ehrlich and Hudda [21], plenty results for different diffusing species such as Re, W, Mo on metal surfaces have been obtained (most of the FIM results are summarized in the comprehensive monography by Ehrlich and Antczak [22]). Unfortunately, FIM is not applicable for studying Li diffusion, since the electric field in a FIM (a few Volts per Angström) removes Li atoms from the surface via field desorption before they can be imaged [23]. In contrary, the scanning tunneling microscope (STM) allows tracing individual atoms and measurements of their displacements at much lower applied fields (at "not-desorbing" polarity) [24]. However, due to the high Li diffusivity, such studies can only be performed at cryogenic temperatures.

For Li-battery applications the diffusion in high-density Li layers, and not that of individual Li atoms, is of main interest. Thus, the surface diffusion at medium ($1 > \Theta > 0.1$, with $\Theta = n_{ads}/n_{substr}$) to high coverages ($\Theta > 1$) should be considered, for which the diffusion occurs as a flux of interacting particles. Such flux can be represented by the first Fick's law as.

$$J = D(\Theta)\, d\Theta/dx, \tag{2}$$

where $D(\Theta)$ is the *chemical* (in the sense "collective") diffusion coefficient (for simplicity, the coverage is assumed to depend only on x). The meaning of such nomination becomes clear, when Eq. (2) is rewritten in a more general form as.

$$J = (D_1 d\mu/d\Theta) d\Theta/dx, \tag{3}$$

with D_1 being a phenomenological transport coefficient [25] and μ being the chemical potential, which depends (apart from coverage) also on temperature and other external parameters. The chemical potential reflects the interaction of diffusing particles and governs the 2D phase transitions in the diffusing layer [25,26]. The $d\mu/d\Theta$ represents the *thermodynamic factor* being responsible for effects such as up-hill diffusion, as will be discussed in more detail below.

To study Li diffusion in high density layers, a local Li deposit can be created on the surface, e.g. using a mask exposing only part of the surface to the adsorbate flux of a Li evaporator [25]. Then, the spatial adsorbate distribution on the surface at different times and temperatures can be monitored by any appropriate technique. The resulting profiles n(x) can be analyzed and the coverage-dependent diffusion coefficient can be extracted using e.g. the Boltzmann-Matano method [27].

For electropositive adsorbates which strongly reduce the work function of the substrate (e.g. Li on most metal surfaces) the spatial adsorbate evolution can be effectively pursued by local work function measurements. Using Anderson's version of the contact potential difference (CPD) and a movable electron gun (for scanning the surface), the work function can be determined with a spatial resolution of ~20 μm and a precision of $\sim 10^{-4}$ eV; thus a "work function surface map" can be constructed by such a "scanning contact-potential microscopy". From the known dependence of the work function on the surface coverage of Li (calibrated independently by e.g. LEED measurements) a Li coverage map can in turn be obtained, with an accuracy of $\sim 10^{-2}$ ML, from which the diffusion coefficient can be determined [25,28]. As a modification of the Boltzmann-Matano method, a strip with a small excess concentration can be deposited on the already homogeneously covered surface and the diffusion caused "diffluence" of this strip can be monitored by scanning work function measurements (Fig. 1a, for details of the evaluation see review [25] and references therein). Using a circular spot-deposit and monitoring its evolution into an ellipse extended along the channels of a furrowed surface (e.g. W(112) or Pt(110)) or along the steps of a stepped surface, the anisotropy of surface diffusion can be studied (Fig. 1b) [28,29].

The spatial evolution of a local excess coverage can be monitored not only by electron beams, as in the discussed work function measurements, but also by scanning the surface with ions or photons [30–36]. The field emission (FEM) and photoemission microscopes (PEEM) can also be successfully applied to monitor the adsorbate coverage evolution [26,37] due to their imaging principle based on the work function of imaged regions. Alkali adsorbates [38,39], particularly Li [40], are particularly useful for such studies, since significant work function changes occurring during the spreading of an alkali layer are immediately reflected in the image contrast of FEM or PEEM. The STM techniques can, of course, also be adapted to measurements of the local work function evolution and thus to the monitoring of surface density profiles [41,42].

The high diffusivity of Li serves as a basis for the *lithium field desorption microscope* (Li-FDM) which can also be used for studies of surface diffusion. In this device the (nearly atomically resolved) image of a sample (usually a nm-sized tip) surface is formed by Li^+ ions field-