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Challenges for lithium species identification in complementary Auger and X-ray photoelectron spectroscopy

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HIGHLIGHTS

- Deeper understanding of the artefacts occurring in AES for investigations of Li metal at battery anodes.
- Following the electron beam induced changes during AES measurement by XPS.
- Possible ways to control electron beam damage are proposed.
- Local distribution of different Li compounds can be displayed by scanning Auger microscopy (SAM).

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ABSTRACT

The combination of high spatial resolution and near-surface chemical information makes Auger electron spectroscopy (AES) a powerful tool for comprehensive surface analysis. The recent interest in lithium metal as an active material in lithium sulphur or lithium air batteries increases the demand for a thorough knowledge of the reactions happening at the electrode interface. Applying AES to the complex surfaces of batteries, however, requires a detailed understanding of the interactions occurring with the highly reactive materials during investigation, especially when using metallic lithium with its passivation layers formed even under glove box atmosphere.

The article is focused on the influence of electron beam damage and residual gas under ultra-high vacuum conditions on the observations made. Immediate irradiation effects are shown to highly depend on electron dose leading to misinterpretation the surface composition and a non-sufficient stability of the sample. The results are further supported by coupled X-ray photoelectron spectroscopy (XPS) measurements that help to understand the beam induced phenomena.

An improved output of the spectroscopic measurement could be achieved employing AES mappings. This allows an improved insight into the local distribution of different lithium compounds in the material surface and can also be applied to other battery active materials.

1. Introduction

The (electro-) chemical reactions between the solvents of the electrolyte and the active material during the first charging and discharge cycles determine the structure and the composition of the interfaces in a lithium ion battery (LIB). In turn those internal surfaces like the so-called solid-electrolyte-interphase (SEI) [1,2] on the battery anode have a large effect on the performance and the lifetime of the battery. To understand the mechanisms and the critical parameters which influence the interface formation, various (surface) analytical tools are needed. In order to go beyond the limited lateral resolution of common analysis tools like X-ray photoelectron spectroscopy (XPS) [3,4], the use of Auger electron spectroscopy (AES) is promising. In particular, the investigation of lithium plating is a highly demanding task for AES. This local formation of metallic lithium (lithium dendrites) is an unwanted process during charging of the battery. Especially, when using metallic Li as anode material [5], which is considered in Li–S batteries [6], the formation of dendrites and its suppression has to be understood. However, a direct observation and identification by other techniques like energy dispersive X-ray spectroscopy (EDX) [7] is challenging and encourage the interest to apply AES on LIB systems.

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In comparison to XPS, AES is a rarely used technique in the field of LIBs. Nevertheless, the existing studies show the potential of AES and how the information about the chemical state and its lateral and depth distribution can contribute to the understanding of LIBs. Beside the depth profiling of several reaction layers of Li foil and different electrolytes [8], the oxidation of metallic Li under UHV conditions were studied and imaged by scanning Auger electron microscopy (SAM) [9]. Additionally the lithiation of silicon [10] and graphite [11] electrodes were investigated by AES. Since the early days of AES, the extraordinary Auger mechanisms of a [He] $2s^1$ electron configuration with its inter-atomic transitions caused a lot of theoretical and experimental [12–15] research efforts.

Additionally in order to study the limits of AES, alkali metal halide systems like LiF were under intensive review [16]. It was shown that the use of electrons for excitation in AES can modify the composition of the investigated surface. Since AES is a very surface sensitive technique, changes of the outermost layers of the sample can be observed. It is also not hard to conceive that the use of electrons for excitation can cause damage of the surfaces [17]. Processes like dissociation and de- or adsorption of excited species have to be considered [16,18]. Moreover the field-induced migration of mobile ions during AES measurement [19] is a possible mechanism which changes the surface composition. It is also conceivable that the energy deposited in the sample causes heating which is proportional to the beam power (I_b * E_b) [20]. This change in temperature can also influence the de-adsorption or diffusion processes. Beside this, the electron dose is an important parameter to describe how many electrons reached the surface being related to how long a certain area of the surface was irradiated with a specific probe current. Hence, a variation the size of the investigated area changes the electron dose absorbed for one Auger spectrum.

Summarized, this means that by varying the AES parameter like probe current (I_b), excitation energy (E_b) or the size of the investigated area it is possible to distinguish between changes of the surface composition induced by electrons, heat or the UHV conditions itself.

Beside the influence of the measurement conditions on its outcome it turns out that the detection of lithium itself by AES is quite challenging. This is not only due to the low intensity of the Li Auger peak but also because of its position at a kinetic energy of around 50 eV in a large secondary electron (SE) background. This leads to a low signal-to-noise ratio which makes longer measuring times necessary. This, on the other hand, means that a larger amount of electrons is needed and the risk of electron damage increases. In addition, the bad conductivity of almost all lithium compounds leads to disturbing charging effects. However, before starting the investigation of complex SEI surfaces or the formation of lithium dendrites a measurement of standard SEI components like Li_2O and Li_2CO_3 is needed. In contrast to XPS the use of standard powders of these materials is not useful in AES. The charging effects on almost all lithium compounds are difficult to manage even with additional charge compensation by positively charged Ar^+-ions. Therefore, to prevent this extra influence on the results, the preparation of thin standard material films on a conductive substrate is considered in this work. The native film on lithium metal [21] provides such a system, which also depends on the surrounding atmosphere. Nevertheless, it is not only a model system for the SEI, but also for the investigation of metallic lithium dendrites.

Since most of the common Li species can be distinguished or identified by XPS, a combination of both techniques in the same machine will consolidate the findings obtained by AES.

Considering all these different aspects, this work attempts to gain closer insight into the factors affecting the stability and the ability to distinguish different lithium containing surfaces by AES and what that can be concluded for investigations of real SEI surfaces. Especially the discussions about the measurement induced formation of elemental Li will show the capabilities and the limits of AES concerning the dendrite formation in LIBs.

2. Experimental

2.1. Surface preparation

The investigated material was a commercial lithium foil (Chemetall) as it is used for electrode materials in Li-metal batteries, which was transferred from a glove box (less than 1 ppm O_2 and H_2O) to the analysis chamber (base pressure $1*10^{-7}$ Pa) by a transfer vessel (JEOL) under Ar atmosphere. This initial state of the lithium foil is hereinafter referred to as fresh lithium foil. This fresh lithium foil commonly has a native surface layer consisting of several different lithium compounds [21]. Ar^+-ion sputtering allows to obtain depth profiles and to change the surface composition. The high reactivity of lithium, mentioned above, makes it also possible to change the surface composition by scratching the foil under specific atmosphere [22].

2.2. Surface analysis

All spectroscopic experiments are performed in a JEOL JAMP 9500F Auger Microprobe with a base pressure of $1*10^{-7}$ Pa. The hemispherical analyser of the system and the attached Mg/Al X-ray source (SPECS XR 50, here operated at 300 W), allows AES as well as XPS measurements on the same sample.

Since the XPS system is not provided in the standard JAMP 9500F system, a calibration of the energy scale with a Cu reference sample was performed ($Cu2p_{3/2}$ at 932.7 eV). The Al K_α-ray beam is reduced by a cone-like collimator and irradiates an area of about 3*3 mm. The photoelectrons are analysed in Fixed Analysing Transmission (FAT) mode with a pass energy of 50 eV.

The Schottky field emission source of the 9500F system is operated between 0.5 and 30 kV and is able to achieve beam currents up to 500 nA. The standard parameters for the Auger measurements were 10 kV with a probe current of 10 nA. The Auger electrons were analysed in Constant Retarding Ratio (CRR) mode with a retarding ratio of 0.32.

In all local AES measurements the beam current was held constant and the electron dose per spectrum was changed by scaling the investigated area.

3. Results and discussion

3.1. XPS and local AES investigations on fresh Li foil

The XPS spectra of the initial surface (Fig. 1 a) of the fresh lithium foil mainly exposes three elements: oxygen, carbon and lithium. A small amount of fluorine is also detected (<3 at.%) which is neglected for the following considerations. The O1s peak at 534 eV and the Li1s at 58 eV can be identified as Li_2CO_3 or LiOH [23]. The additional C1s peak at 292 eV and the results from quantitative analysis with standard relative sensitivity factors (RSFs) [24] [25] makes it likely that all the Li and O is bounded in Li_2CO_3 at the surface. The second C peak at 287.5 eV corresponds to C—C or C—H compounds on the surface.

Since the calibration of the binding energy scale is challenging [26], it should be noted that the XPS spectra are not shifted to a specific reference energy, because at the Li foil no surface charging was observed. This should be considered when comparing absolute values of the binding energies with literature mostly using C1s at around 285 eV for energy referencing.