



Li_xV₂O₅ – Analysis of surface reactions by spectroscopic quartz crystal microgravimetry



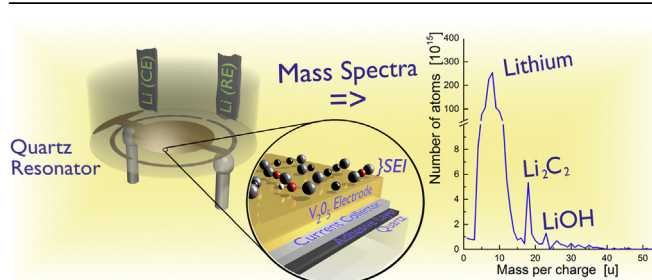
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HIGHLIGHTS

- Thin Li_xV₂O₅ layers (40 nm–302 nm) were prepared by ion beam sputtering.
- Layers are investigated via in situ electrochemical quartz crystal microgravimetry.
- Time-resolved in situ mass spectra are obtained from the measurement results.
- Electrochemical reactions during the uptake/release of lithium are studied.
- Different chemical species are identified, which are involved in the SEI formation.

GRAPHICAL ABSTRACT



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ABSTRACT

We investigate the electrochemical side reactions that occur during the cyclic lithiation/delithiation of sputter-deposited Li_xV₂O₅ films. For this purpose, the mass change of Li_xV₂O₅ films during lithiation/delithiation is measured by quartz crystal microgravimetry, while the electrical charge that is flowing during this reaction is measured by cyclic voltammetry. A time-resolved evaluation of the measurement data, in combination with an advanced type of data processing, finally allows us to calculate time-resolved quantitative mass spectra. These spectra provide information about the chemical species that take part during the electrochemical reactions. Based on this technique, we study the electrochemical side reactions between the Li_xV₂O₅ and the corresponding liquid electrolyte, i.e. we investigate the time-resolved formation of the solid electrolyte interface (SEI) layer during long term cycling. We are able to identify several chemical species that are formed during cycling and moreover, we identify three different stages of SEI formation.

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1. Introduction

When trying to understand and improve the electrical performance of secondary batteries, interface reactions between the electrodes and the liquid electrolyte are of strong relevance. Here,

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the so-called solid electrolyte interface (SEI) layer is of particular importance [1,2]. This SEI layer is usually formed during the first charge/discharge cycles at the surface of the electrodes and strongly influences the electrical characteristic of the batteries: For instance, in order to form the SEI, mobile lithium ions are partially consumed by irreversible chemical reactions, causing a capacity decrease of the overall electrochemical cell. Moreover, the SEI may act as a diffusion barrier for lithium ions, causing an increase of the

overall cell resistance and thus a decrease of the maximum charge/discharge power [2].

Consequently, a fundamental understanding of SEI properties is essential in order to control e.g. the composition and the thickness of the SEI, and to optimize the electrical performance of lithium ion batteries. Hence, several groups studied SEI formation in the case of different kinds of electrode materials and electrolytes, respectively. To this aim, various *ex situ* techniques have been applied, like induced coupled plasma analysis [3], scanning electron microscopy [3,4], or infrared spectroscopy [3]; as well as different *in situ* methods, like X-ray diffraction, atomic force microscopy [5], or electrochemical impedance spectroscopy [3,4].

In general, *ex situ* techniques usually provide only some kind of 'snapshot' of the electrode and its surface. But they do not allow a time-resolved investigation of the SEI, although this is the key to understand the chemistry of the formation process. Moreover, results of *ex situ* measurements need to be considered with care, due to the quite low chemical stability of some interface reaction products. This low stability causes a degradation of SEI components during preparation or the following measurement and may thus lead to misleading results.

In contrast to *ex situ* techniques, *in situ* experiments allow a continuous, time-dependent characterization of the SEI formation, and results of these experiments are per se not influenced by any secondary temporal degradation of the interfaces. However, *in situ* techniques usually require an increased experimental effort, and it has to be taken into account that the measurement procedure itself may influence the properties of the SEI. Therefore, *in situ* techniques are required that provide detailed information about chemical and physical properties of the SEI layer, but do not influence the SEI formation. These requirements are well met by the *in situ* quartz crystal microgravimetry (QCM) [3,4,6–9], which has been applied in the presented work.

In the recent past, QCM has gained immense attention in various fields of science, like high-temperature calorimetry [10], biochemistry [11], or electrochemistry [6,9]. The reason for this broad field of applications is that QCM allows a precise measurement of mass changes within the range of some nanograms under broad variation of the experimental conditions. Thus, if used in battery science, QCM may allow an accurate determination of the mass change of an electrode during its oxidation/reduction reaction. For this purpose, QCM is usually combined with electrochemical techniques, like chrono potentiometry or cyclic voltammetry (CV).

Such electrochemical QCM *in situ* experiments have already been carried out by other authors, e.g. in case of the lithiation/delithiation of carbon [8], tin [7], V_2O_5 [5,12,13], $LiCoO_2$ [3], or $LiMn_2O_4$ [4]. Within these works, some significant discrepancy between the measured change of mass and the inserted/extracted electrical charge has been observed, clearly indicating some significant electrochemical side reactions. Moreover, *in situ* electrochemical QCM was also used to study the species, that are intercalated/deintercalated in V_2O_5 electrodes [14,15], finding that at high scan rates charge compensation is not only carried out by Li^+ [14], but also by small amounts of accompanying solvent. However, these previous studies usually investigate only a few charge/discharge cycles and to the best of our knowledge no detailed long-term data are available. Thus, only minor is known about the cycling dependence of the SEI formation; and moreover, no time-resolved identification about individual reaction products is available, since this is usually not directly accessible via QCM.

Therefore, in this work we provide a profound combined QCM-CV *in situ* study, to investigate reversible and irreversible reactions that occur during the lithiation/delithiation of crystalline V_2O_5 electrodes. Here, V_2O_5 is chosen since it is known to provide a high

lithium storage capacity of around 400 mAh g^{-1} and an excellent cycling stability [16,17]. Moreover, it is considered as a potential candidate for future all solid state thin film batteries, which is – amongst others – due to the fact that functional V_2O_5 thin film electrodes can reliably be prepared by different experimental methods, like chemical vapor deposition [18] or sputtering [16,19–21].

In order to investigate reversible and irreversible reactions of V_2O_5 during its lithiation/delithiation, we combine the techniques of QCM and CV, as has already been done by other authors [5,12,13]. But in contrast to previous studies, we address three fundamental aspects: (i) We characterize the long-term cycling behavior of V_2O_5 with respect to irreversible side reactions, (ii) we distinguish whether these irreversible reactions take place at the surface of the electrodes or inside the volume, and (iii) we identify the products of the side reactions by a novel type of data evaluation, namely by calculation of quantitative QCM mass spectra.

The latter aspect, i.e. the determination of quantitative mass spectra, opens the unique possibility to carry out *non-destructive*, *in situ mass spectroscopy* on battery electrodes. This may be highly relevant for fundamental research on electrode materials, and to the best of our knowledge it has not been introduced in literature before.

2. Experimental

2.1. Measurement setup

In this work, *in situ* measurements of the mass change during lithium intercalation/deintercalation in V_2O_5 were done by a quartz crystal microbalance (RQCM, Maxtech) in combination with a potentiostat/galvanostat (VSP300, Bio-Logic). For the measurements, a custom-made cell was used that was mounted inside of a glovebox, in order to provide an inert Ar atmosphere during the experiment. A sketch of the setup is shown in Fig. 1 (left).

The electrochemical cycling was carried out by a three-electrode configuration. As reference and counter electrodes two Li strips (Alfa Aesar, $\geq 99.9\%$) were used, while a V_2O_5 layer, sputter-deposited onto a quartz resonator, served as the working electrode. The electrochemical cycling was conducted inside a liquid electrolyte, i.e. a mixture of 50 wt% ethylene carbonate (Sigma-Aldrich, $\geq 99\%$) and 50 wt% dimethyl carbonate (Merck, $\geq 99\%$), containing $1 \text{ mol l}^{-1} LiClO_4$ (Sigma-Aldrich, $\geq 99.99\%$).

2.2. Thin film preparation

The V_2O_5 thin films were prepared by ion beam sputter deposition, using a custom-made sputter chamber, equipped with a 4 cm rf ion gun (Roth & Rau) [20]. During this process, an Ar^+ beam of 900 eV and 2.4 mA cm^{-2} is focused on a target, so target atoms are sputtered-off and deposited onto a substrate. To avoid layer contamination, the sputter process is carried out under ultra-high vacuum conditions at a base pressure of $< 10^{-7}$ mbar. During deposition of the V_2O_5 , Ar (2.8 sccm) was used as process gas and O_2 (1.1 sccm) was added as reactive component. Consequently, the pressure during sputter deposition was about 10^{-4} mbar. The thickness of the deposited layers was measured *in situ* by a quartz crystal micro balance (SQM 160, Inficon), which was initially calibrated by profilometry.

As a sputter target for the deposition of the V_2O_5 , a disk of cold pressed V_2O_5 powder (Riedel de Haen, $\geq 99.5\%$) having a diameter of 8 cm and a thickness of 5 mm was used, while AT-cut quartz resonators (Inficon) of 1" in diameter and 185 μm in thickness served as substrates (Fig. 1, right). On each surface of these quartz resonators a 25 nm Ti layer and a 100 nm Pt layer were deposited

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