



# Lithiation and Delithiation Mechanisms of Gold Thin Film Model Anodes for Lithium Ion Batteries: Electrochemical Characterization



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## ABSTRACT

Lithium Ion batteries have to be significantly improved to fulfill the challenging needs in electromobility or large scale energy storage technology. In this context the use of model electrodes such as single-crystals or thin films allows well-defined mechanistic studies. Here we present a detailed electrochemical investigation of the lithiation–delithiation behavior of Au thin film model electrodes in ionic liquid electrolyte. Cyclic voltammetry, galvanostatic-, stepwise potentiostatic lithiation–delithiation cycles, as well as galvanostatic intermittent titration technique, GITT, measurements were performed. We found nearly identical mechanism of Li insertion and extraction in these three types of measurements at different current levels. The mechanism of alloying or lithiation deviated from the mechanism of dealloying or delithiation. While during the lithiation process two main plateaus related to phase transformations occur in the potential–time curves three main plateaus appear during delithiation. First results of theoretical simulations confirm a high number of possible metastable phases in the Li–Au system. The measurements also point to the influence of SEI-film formation on the cycling behavior. Based on these insights a mechanistic sequence and a phase evolution diagram for the electrochemical alloying of Li with Au are presented.

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## 1. Introduction

Interfacial electrochemistry has often used Gold (Au) substrates as model systems for various aspects of surface science problems, from metal–organic interfaces, such as for example thiol self-assembled monolayers [1,2], (bio)-sensor applications [3–6] or fundamental oxidation studies [7]. The high inertness and ease of sample preparation by flame annealing renders Au an appealing model system for electrochemical studies. Also in Li-ion battery (LIB) research Au is used as coating [8] or (nanoporous) template [9], as well as as model system for bulk electrodes [10,11]. Au seed layers are furthermore employed for Si nano-wire growth for LIB Si anodes and Au is thus an integral part of the respective LIB anode [12]. Lithium (Li) as a small and reactive element diffuses readily in Au bulk materials (similar to Zn [13]), which has been recently employed to obtain Au–Li alloy precursors for further

producing high-surface-area nanoporous gold (npg or npAu) by dealloying [14]. The dealloying approach has been early used to produce Raney Ni [15] or more recently dealloyed core-shell nanoparticles for catalysis [16]. But npAu and other porous elements have in the last years been proposed for a number of further potential applications from actuators and bio-sensors to Li-ion batteries and supercapacitors [9,17]. Such porous electrodes do better cope with the respective immense volume changes involved in alloying reactions. For all these topics a thorough understanding of the chemical, structural and microstructural evolution during alloying and dealloying cycles is necessary.

Electrochemistry embodies mainly integral techniques measuring the changes in an external electrical current or potential originating from macroscopic surfaces. Nevertheless, in combination with well-ordered thin films or single crystal surfaces even atomic scale information can be obtained due to the low electrical currents which can be technically measured and the relatively large effects on potential which even small changes of the solid–electrolyte interface structure may have. Examples are the monolayer adsorbate structures of electrolyte molecules such as sulfate on Au(111) [1,18] or sub-monolayer changes during multistep under-potential

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deposition (UPD) such as Cu on Au (111) [19]. But it is also clear that in most cases additional complementary, potentially in-situ, microscopic information is needed to clarify the true structures and mechanisms [20,21]. Prominent contributions have been hereto provided by electrochemical scanning tunneling microscopy (EC-STM) revealing local atomic and molecular interface structures [21] or by the use of Synchrotron radiation for X-ray absorption spectroscopy (XAS and EXAFS) and in-situ X-ray diffraction [22–25].

This project is part of a more extended ongoing Synchrotron-based in-situ X-ray diffraction study on lithiation and delithiation of pure Au anodes mimicking a model battery charging and discharging process. Next to the inertness of the material, the high cross-section for X-ray scattering renders Au an ideal substrate. The detailed diffraction results will be reported separately. While for frequently time consuming electrochemical diffraction studies often potentiostatic modes are employed, batteries are usually characterized by galvanostatic cycling. Therefore we here thoroughly compare potentiostatic and galvanostatic modes and report next to more common cyclic voltammetry and galvanostatic cycling also less frequently used Galvanostatic Intermittent Titration Technique (GITT) measurements [26].

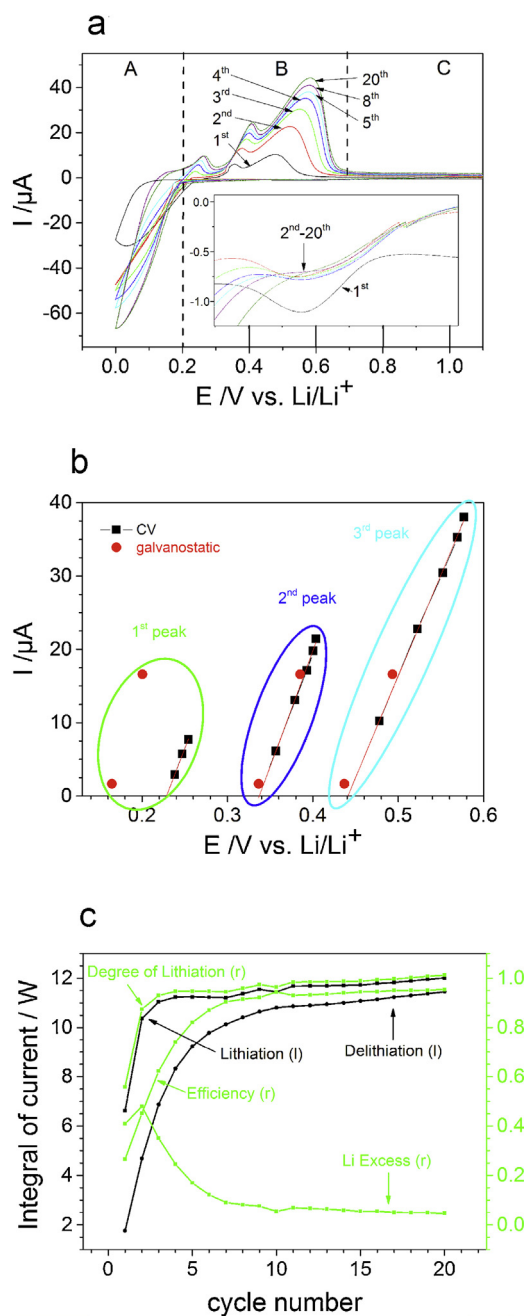
## 2. Experimental

The sample for the presented electrochemical measurements was a 100 nm thin Au-film on a polycrystalline Cu substrate. Cu discs (8 mm diameter, 0.5 mm thickness) were first ground (grain sizes 1000 and 2500) and then polished (using silica particles of 50 nm grain size in basic aqueous suspension). The Au film was applied by RF magnetron sputtering in Ar atmosphere at room temperature at a deposition rate of 1 Å/s. The Au target was supplied by Kurt J. Lesker Company Ltd., England, and the deposition was controlled by an Inficon IC6 deposition controller (Inficon, Switzerland).

The electrochemical measurements were carried out in a custom made electrochemical Teflon cell allowing a spot of the sample of 4 mm in diameter to be in contact with the electrolyte. Li foils (Kisco Ltd. Japan) served as counter and reference electrode. The electrochemical cell was assembled and operated inside an Ar-filled glovebox (SylaTech GmbH, Germany) with O<sub>2</sub> and H<sub>2</sub>O contents below 1 ppm. The electrolyte used was a 0.3 M solution of the Li-salt LiTFSI (Merck KGaA, Germany) in the ionic liquid Pyr<sub>14</sub>TFSI (1-butyl-1-methylpyrrolidinium-bis(trifluoromethanesulfonyl)-imide) [27] (Solvoionics, France). We used an Ivium Compact Stat potentiostat (Ivium Technologies B.V., Netherlands). CVs were acquired between 1 V and 0 V vs. Li/Li<sup>+</sup> at a potential scan rate of 1 mV/s. Galvanostatic lithiation–delithiation cycles were performed at different currents. At 1.7 C (16.6 μA) the cell was cycled between 1.0 V and 5 mV and at 0.17 C (1.66 μA) between 1.5 V and 5 mV. Galvanostatic Intermittent Titration Technique (GITT) measurements [26] were conducted at 0.17 C alternating between 1000 s of galvanostatic lithiation and delithiation and 2000 s at open circuit potential (OCP) at each step. Potentiostatic lithiation–delithiation cycles in a potential range between 1.5 V and 5 mV were performed by stepwise lowering and raising the potential to avoid large currents. The next potential step was triggered with the current undercutting a set respective limit. In case of the measurements employing a 5 μA current limit the step size was 0.1 V between 1.5 V and 0.3 V during lithiation and between 0.5 V and 1.5 V during delithiation. In the potential range below the potential step size was 20 mV. Employing a current limit of 1 μA the potential step size was 0.1 V between 1.5 V and 0.3 V during lithiation, between 0.5 V and 1.5 V during delithiation, and 10 mV otherwise.

## 3. Results and Discussion

All electrochemical measurements presented here have been obtained from a sputter-deposited 100 nm thin Au film on a polycrystalline Cu substrate. The electrolyte was a 0.3 M solution of LiTFSI in Pyr<sub>14</sub>TFSI and the reference electrode commercial Li foil.



**Fig. 1.** (a): Cyclic voltammograms of a 100 nm thin Au film in the voltage range from 0 V to 1.5 V vs. Li/Li<sup>+</sup>. (b): Pairs of peak-potential and peak-current values of the three anodic peaks from Fig. 1a extracted from the first five CV cycles (squares). For the first anodic peak the values are given starting from the third cycle. The circles represent the respective values of the galvanostatic lithiation–delithiation cycles from Fig. 2a. (c): Lithiation–delithiation efficiency during CV measurements. The letters in brackets denote the associated scale: (l): left, (r): right. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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