LITHIUM ION INTERCALATION INTO THIN FILM ANATASE

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1. Introduction

Development of new battery systems is an ongoing challenge. Common electrodes for lithium ion systems are made from pressing bulk powders, including binders and conductive additives. Bulk electrodes have several negative characteristics mainly caused by their construction from powders. Therefore new approaches to electrode design and construction are finding their way into research. Several of these new approaches, for example on chip grown integrated micro batteries, require the use of conformal thin films. Atomic layer deposition(ALD) is showing itself as the technique capable of delivering the conformity and composition necessary. For example TiO_2 [2] in its anatase form is a prospective material for lithium ion intercalation, as shown by its characteristics and governing equation.

$$Li_xTiO_2 \iff Li^+ + e^- + TiO_2 \tag{1}$$

1.Negligible volume change
2.Intercalation constant x in equation[Eq.1] depends on dimensions and phase of the film.
3.Relatively low specific capacity of anatase, 335 mAh/g for $x = 0.5$.
4.Optimized ALD processes to deposit anatase TiO_2 are available.

Other prospective examples of materials include SnO_2 [1] with its extreme volume change and V_2O_5 [3] with comparable properties to anatase. Studying conformal thin films grown by ALD on various substrates in lithium ion battery systems is ongoing and paralleled with development of recipes for lithium containing films made by ALD [4].

The aim of this work is to find the optimal parameters for thin film TiO_2 anatase grown by ALD for use as electrode in lithium ion batteries. Two parameters, the optimal film thickness and growth conditions are aimed for. Optimal film thickness for achieving optimum between capacity gained from volume and capacity gained by changing of the intercalation constant and optimal growth conditions for film conformity on structured substrates with high aspect ratio. Here we presents first results from this ongoing research and discuss future outlooks.

2. Experimental setup

A suitable container was rigged for sustaining argon atmosphere and low humidity. Glass vessel sitting inside the container contains the sample system with wire leads being sealed into the container. Working electrode consists of cold pressed $LiMn_2O_4$ with aluminum powder, reference electrode consists of a lithium metal pellet. Electrolyte consists of 0.5 mol solution of $LiClO_4$ in propylene carbonate. Electrodes are separated by distance of $d = (1 \pm 0.2)\,cm$.

Samples are polished aluminum disks coated with ALD using titanium isopropoxide and ozone at $573\,K$. Film thicknesses of 4 and 8 nm were aimed for, thicknesses were measured on a silicon standard. The premise is that these values do not divert more than 10 % due to the nature of ALD deposition. Phase of grown film was that of polycrystaline anatase.

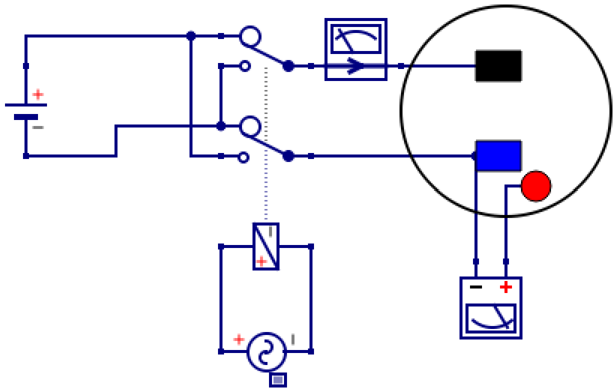
Keithley 196 system DMM and Agilent 34401A are used to measure the time dependencies of voltage and current in the setup. A stabilized voltage source provides driving voltage. Switching between charging and discharging is done by an electromagnetic relay and GPIB controlled DC source.

First setup [Fig.1a] was used as sensor for measuring changes in electrochemical potential of samples coated with thin films of anatase against reference electrode, in this case the current measure was informative and information about overall energy balance was inaccurate.

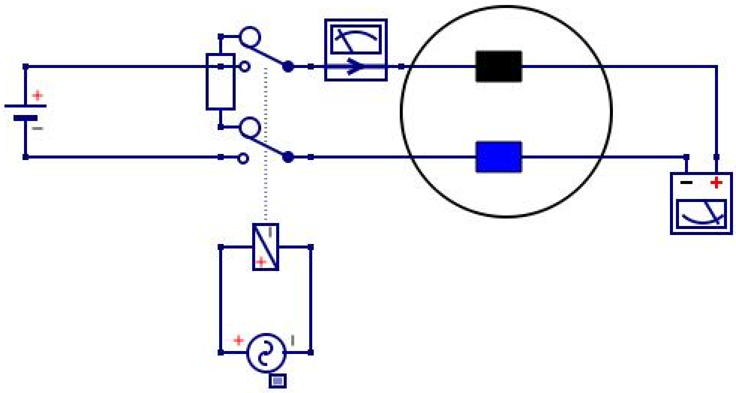
Second setup [Fig.1b] was used to measure energy of discharge as precisely as possible.This was achieved by discharging the system into a high resistance while the DC source was galvanically separated from the circuit. In this setup reference electrode was not used, as it may be a potential secondary source of ion movement against working electrode. Overall energy of discharge was computed from P(t) data which were numerically integrated and discharge cycles were selected. Charge cycles were discarded as the DC source can support parasitic reactions.

Fig. 1: *Experimental setup*

(a) *Electrochemical potential measurement*



(b) *Resistance discharge*



3. Main results

Firstly we have measured the changes in electrochemical potential of samples during intercalation/deintercalation of lithium ions, as is shown on [Fig.2]. From these measurements we have determined the detection limit of our apparatus to be below 4 nm of anatase. Then we proceeded with long term measurement of energy gained during discharge [Fig.3], which is directly proportional to x and amount of anatase film [Eq.1]. Formation of solid electrolyte interface (SEI) was observed by naked eye and subsequently confirmed to be amorphous by x ray diffraction [Fig.4].

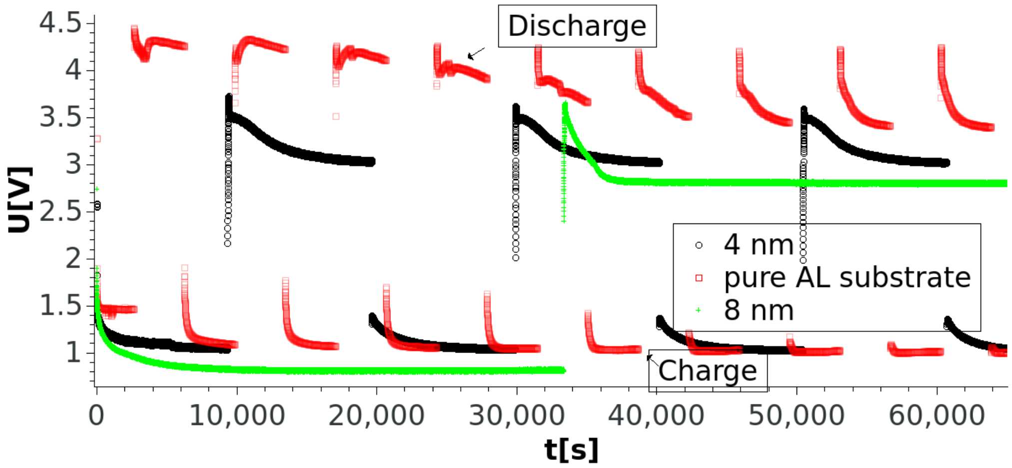


Fig. 2: *Plots of electrochemical voltages of sample against reference electrode. The ability to distinguish between substrate and coated sample is clear from the shape of the functions. The time of cycle for 8 nm sample was prolonged to show the saturation from maximum of x to its minimum.*

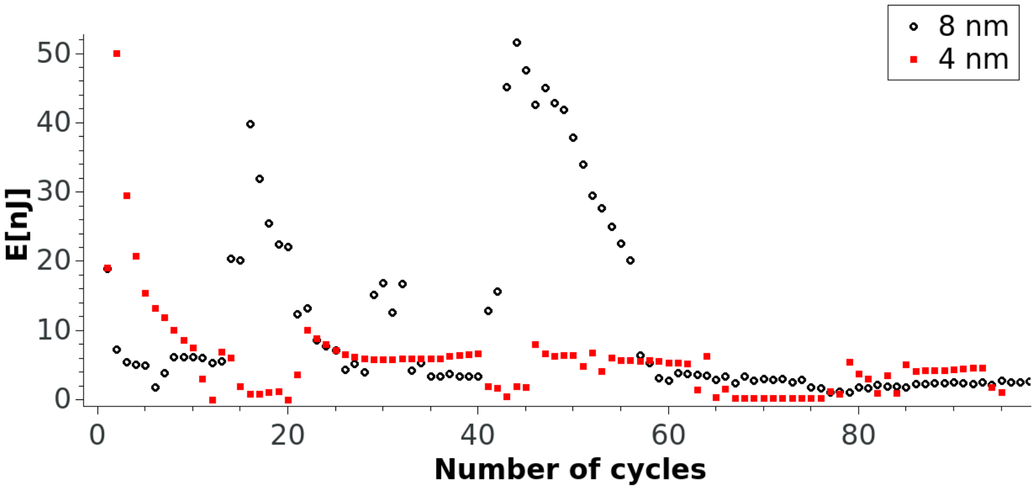


Fig. 3: *Shows the work the system has done during its return to equilibrium. Charging was at* U_{out} = (2.02±0.03) *V for 2 hours and discharge was done into a resistance* R = (1550±15.5) Ω *for the same time.*

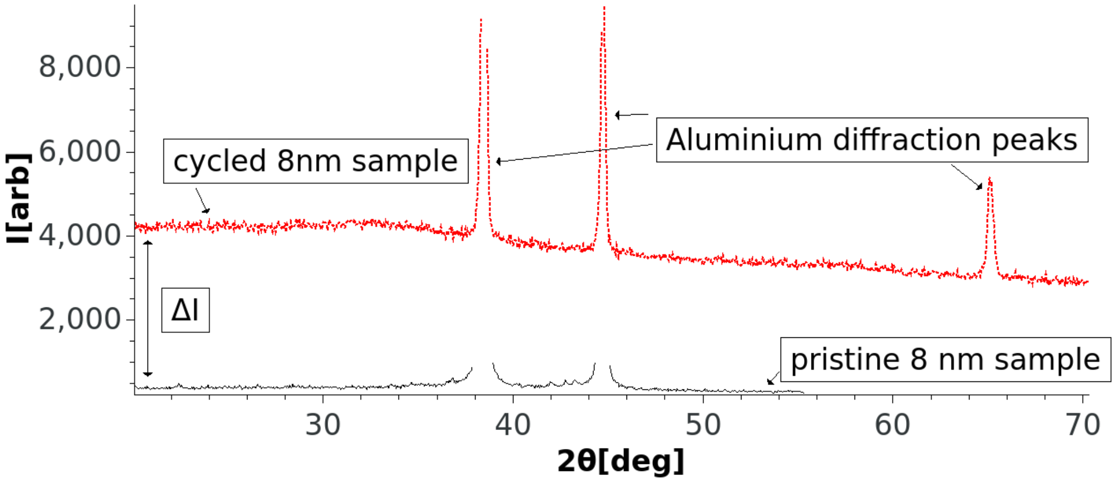


Fig. 4: *X ray diffraction data (grazing incidence method) for cycled and pristine samples, both samples were coated at the same time. Amorphous nature of created SEI film is visible from the difference in intensity* $\triangle I$.

4. Discussion

The measure of electrochemical potential, while showing small differences between thicknesses of anatase films, clearly allows to distinguish between coated samples and pure substrates. This ability starts to falter at films of thicknesses of 3 nm and lower.

Energy of discharge shows unexpected periodic behavior, which cannot be explained by relative error of the measurement apparatus as this is on the order of $\Delta\varphi \approx 10^{-2}\,\%$, and the relative error for volume of anatase film is approximately $\triangle\varphi \approx 10\,\%$. Explaining these rather sudden and large shifts, which have periodical behavior has to be a part of our future outlooks. However from the last few cycles, therefore weighting the estimate down, we can estimate the intercalation constant for 4 nm sample as $x \approx 0.6$ and 8 nm sample as $x \approx 0.3$. Therefore we have a strong indication that 8 nm and thicker films are not necessary.

An solid electrolyte interface was clearly created during cycling of the system, the optical difference was visible by naked eye. X-ray grazing incidence confirmed the amorphous structure of this films and it is a future outlook to measure its composition.

A last outlook is to quantify the expansion of anatase upon intercalation by X-ray diffraction, as this was problematic on the aluminum substrates.

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