



# Nanoscale electrochemical measurements on a lithium-ion conducting glass ceramic: *In-situ* monitoring of the lithium particle growth

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## ABSTRACT

We performed nanoscopic cyclic voltammetry and chronoamperometry on the *Ohara* lithium ion conductive glass ceramic. When the critical bias voltage was exceeded, metallic lithium particles were deposited irreversibly under the conductive AFM tip acting as working electrode. Due to the huge area difference between working electrode and counter electrode, a reference electrode was not required. We present an *in-situ* method for studying the particle growth mechanism by simultaneously monitoring the reduction current and the particle height. We found good agreement between the topographically determined volume of the lithium particles and the volume expected from the charge flow. The results for time dependence of the particle growth can be used for controlling the vertical and lateral dimensions of the particles.

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## 1. Introduction

Solid lithium ion conductors are of great interest for solid-state lithium batteries and for lithium-air batteries. Besides high lithium ion conductivity and broad electrochemical stability window, the absence of toxicity is required [1]. The *Ohara* lithium ion conductive glass ceramic (LIC-GC) [2] is of special interest for lithium-air batteries due to the relatively high room temperature conductivity in the range from  $10^{-4}$  to  $10^{-3}$  S/cm [3] and the long-term stability against water and aqueous solutions of lithium salts [4–6]. The glass ceramic consists of NASICON-type crystalline grains (Li-Al-Ti-Si-P-O) with sizes of about 140 nm and of impurity phases, in particular  $\text{AlPO}_4$  [7]. Therefore, the ion transport properties and the electrochemical properties of the LIC-GC are expected to be heterogeneous on nanoscopic length scales.

Such heterogeneous properties can be probed by means of electrochemical AFM techniques. Here, a conductive AFM tip acts as the working electrode. Due to the huge area difference between the AFM tip and the counter electrode, the voltage drops completely at the working electrode [8]. Therefore nanoscopic measurements can be carried out in a two-electrode setup, thus avoiding the use of reference electrodes.

Kalinin and coworkers [9] performed nanoscopic cyclic voltammetry (CV) on the LIC-GC in contact mode and detected non-zero current responses when negative bias voltages exceeding 5–8 V were applied to the conductive AFM tip. The reduction current was assigned to the formation of Li metal particles, a finding supported by topographic imaging. Kalinin and coworkers calculated the ratio of lithium metal atoms to the number of electrons which had flown through the tip and obtained a value of 0.75. The lack of an oxidation peak in the CVs demonstrated the irreversibility of the formation of the reaction product at ambient conditions.

Voltage-biased AFM tips can also be used for the nanopatterning of solid surfaces. Lee and coworkers [10] generated nanopatterns of metallic silver particles in sub-100 nm range on the surface of the solid silver ion conductor  $\text{RbAg}_4\text{I}_5$ . Garcia and coworkers [11,12] described a non-contact local oxidation of metal and semiconductor surfaces involving a bias-induced liquid meniscus between the tip and the sample surface. Terabe et al. [13] produced a nanoscale line structure on a silicon sample surface using an ionic/electronic mixed conductor tip of a scanning tunneling microscope as a metal atom source.

In this paper, we study the tip-induced particle growth mechanism by means of nano CVs and nano-chronoamperometric measurements using the LIC-GC as a model material. From the measured charge flow, the theoretical particle volume could be determined as function of bias voltage or time. Simultaneously, data for the particle height were

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acquired, so that the lateral particle radius could also be calculated. Thus, by simultaneously recording the current and the particle height, we have got a method for *in-situ* monitoring the particle growth. While the current is a measure for the growth rate of the particle, the geometrical parameters (height, lateral radius, volume) are an integral measure for the particle growth.

In ambient conditions, it seems likely that metallic lithium reacts immediately with ambient moieties like  $O_2$  and  $H_2O$  etc. In order to investigate the influence of such processes, comparative measurements in ultra-high vacuum (UHV) were performed.

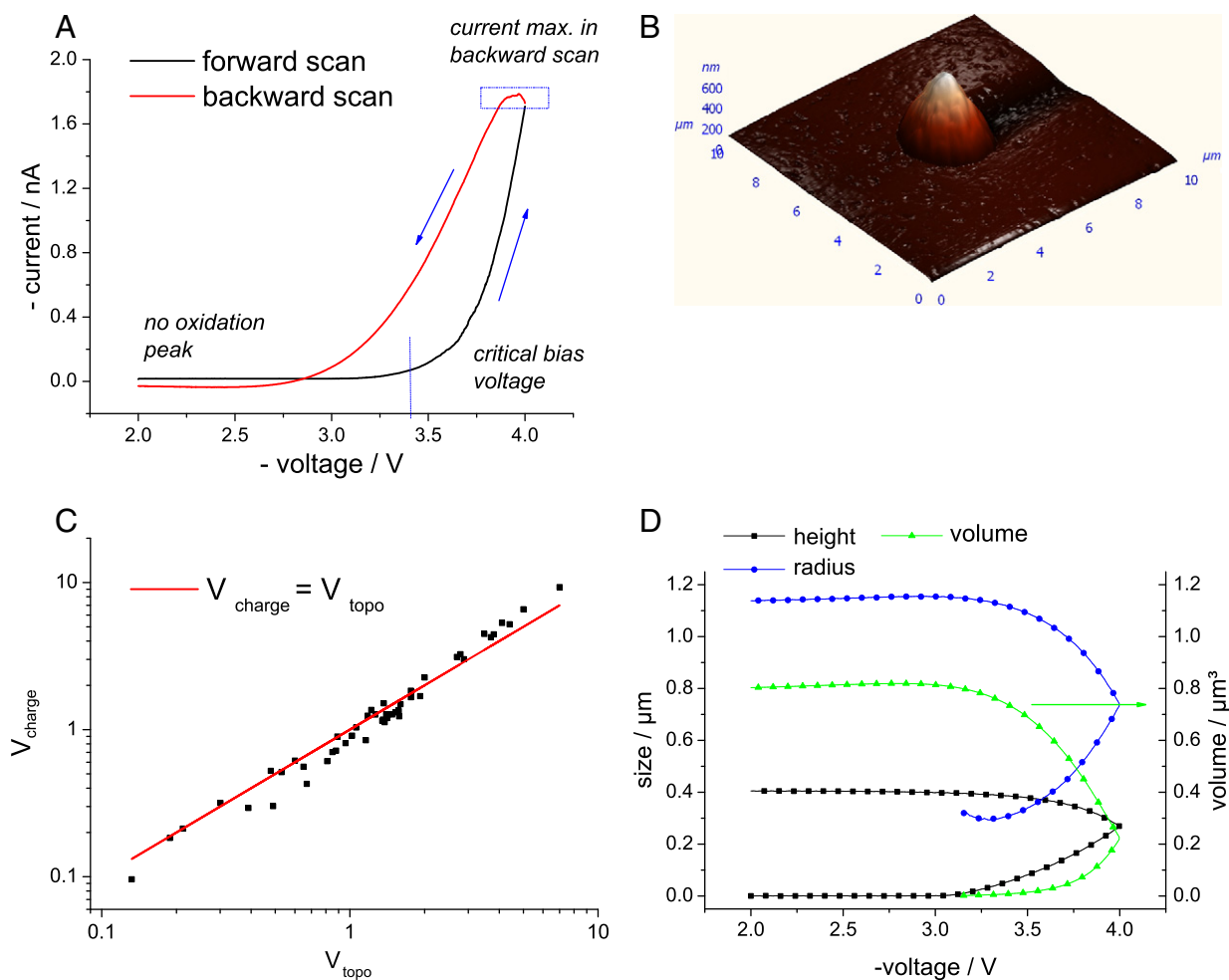
## 2. Experimental

A commercially available *Ohara* LIC-GC plate with a thickness in the range of  $150\ \mu\text{m}$  was used for the nanoscopic electrochemical measurements. A Pt electrode (area  $\sim 0.04\ \text{cm}^2$ ), acting as counter electrode, was sputtered onto the face of the sample that was subsequently studied with the AFM tip. The nanoscopic measurements under ambient conditions were performed using a *NT-MDT-Solver P47* atomic force microscope with a conductive tip acting as working electrode. To obtain reproducible results, the usage of cantilevers with high spring constants in the range of  $40\ \text{N/m}$  was necessary. We chose conductive diamond coated cantilevers (*Nanosensors GmbH*, CDT-NCHR). The electrochemical

measurements were performed in contact mode with tip/sample forces in the range of  $1\text{--}2\ \mu\text{N}$ .

Before starting an electrochemical measurement and again after completion of the measurement, topographic surface imaging was performed in tapping mode over an area of typically  $5\times 5$  or  $10\times 10\ \mu\text{m}^2$ . The topographical volume of the particles as well as the lateral and vertical dimensions were analysed by the *Gwyddion* software after applying a plane correction to the topographic images. All experiments were repeated several times for different positions of the tip on the sample surfaces in order to obtain statistically significant results. The cyclic voltammograms were recorded by using the internal voltage source of the AFM in constant height mode. The deflection was converted into the height using a deflection-height calibration curve. After completion of an electrochemical measurement, a topographic image of the lithium particle was taken, and the particle height was compared to the value obtained from the calibration curve. This comparison was then used for a correction of the particle height during the growth process. Due to limitations of the photo diode, the height should not exceed values of  $500\ \text{nm}$ .

For the chronoamperometric measurements, the AFM was connected to a Novocontrol Alpha-AK impedance analyser equipped with a POT/GAL 15 V/10A electrochemical interface. These measurements were carried out in constant-force mode so that the height



**Fig. 1.** A: Nanoscopic cyclic voltammogram of the *Ohara* lithium ion glass ceramic (LIC-GC) obtained with a scan rate of  $200\ \text{mV/s}$ . The scan direction is marked with arrows. The critical bias voltage required for particle deposition is marked with a dashed line. Remarkably, the current maximum (dashed square) is located in the backward scan. A re-oxidation peak is absent. B: Topographic image of a lithium particle acquired in tapping mode. The image is plane-corrected. C: Plot of the topographical volume  $V_{\text{topo}}$  versus the charge-based volume  $V_{\text{charge}}$ . The line is drawn to guide the eye. D: Vertical (black squares) and lateral (blue dots) dimensions of the lithium particles as well as charge-based volume (green triangles, left scale) as function of the tip voltage during forward and backward scan.

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