AFM tip-induced metal particle formation on laser-structured and on unstructured surfaces of solid-state ion conductors

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ABSTRACT

Metal particles were deposited on the surface of solid-state ion conductors by means of a negatively biased AFM tip, and the deposition process was probed by combining chronoamperometric measurements with topographic imaging. It was checked whether the metal particles can act as local electrodes for measuring the local conductivity of the solid-state ion conductor. We found that metallic silver particles on the surface of silver-ion conducting glasses work perfectly as electrodes, even at cathodic voltages below -1 V. In contrast, lithium particles deposited on a lithium-ion conducting glass ceramic (LIC-GC) measured a nanoscopic conductivity which was considerably lower than the macrosocopic conductivity. This is most likely due to the fact that the LIC-GC is not stable against metallic lithium, so that a resistive layer is formed at the interface. The surface of the silver-ion conducting glasses was additionally modified with tracks using a laser ablation technique. The sharp edges of tracks triggered the silver deposition, so that metallic silver could be arranged in bands with lateral extensions of about 50 µm, when cathodic voltage pulses in the range of -0.4 to -0.6 V were applied for a period of 1 s or even less.

1. Introduction

Solid state ionic conductors play a crucial role for the application in battery devices [1]. They show several advantages over liquid electrolytes, such as high thermal stability, absence of evaporation and leakage and the opportunity for thin film preparation. Besides a broad electrochemical window and the absence of toxicity, a high ionic conductivity is required. The Ohara lithium ion conductive glass ceramic (LIC-GC) [2] is a suitable solid electrolyte for lithium-air batteries due to its ionic conductivity in the range of 10^{-4} S/cm [3] and its stability against water and aqueous solutions of lithium salts [4–6].

If solid ion conductors are structurally heterogeneous, spatially resolved studies of their electrical and electrochemical properties are highly relevant. Recently, different scanning probe microscopy techniques were applied for studying local properties of solids and solid electrolyte interfaces with high resolution. Balke et al. [7] used electrochemical strain microscopy for probing lithium ion diffusion in $LiCoO_2$ with a resolution of about 100 nm. In this technique, the application of an electrical potential to the AFM tip leads to a redistribution of lithium and to a deformation of the material which is directly probed. An interesting approach for visualizing the formation of nanosized metallic silver clusters on superion conducting $RbAg_4I_5$ film was reported by Valov et al. [8]. By doping $RbAg_4I_5$ with 0.1 at.% Fe, they increased the

electronic conductivity of the silver ion conductor to a level sufficient for STM imaging. Short voltage pulses applied to the tip led to the formation of the Ag clusters, and the underlying processes were studied with high lateral, mass and charge resolution. Lee at al. [9] presented an electrochemical nanopatterning technique on $RbAg_4I_5$ using atomic force microscopy. By applying short negative voltage pulses to the AFM-tip, nanometer sized silver depositions were locally formed at the tip. They investigated the effect of the amplitude and the duration of the voltage pulse on the size and the shape of the deposited silver clusters. Morales-Masis et al. [10] carried out a nanoscopic Hebb–Wagner polarization experiment on a resistive switching device. This device consisted of a mixed conducting Ag_2S thin film contacted by an ion-blocking Pt-coated AFM tip and a large-area reversible Ag reference electrode. Current-voltage curves at tip bias voltages below the critical switching voltage provided local information about the steady-state electronic transport in the Ag_2S film.

Despite these works, there is still a lack of knowledge about methods for quantitative measurements of nanoscale electrical and electrochemical properties. Recently, we used atomic force microscopy to carry out quantitative nanoscopic impedance measurements on silver-ion conducting phosphate glasses with different amounts of AgI [11]. Doping silver phosphate glasses with AgI increases the conductivity from 10^{-7} S/cm for pure $AgPO_3$ to 10^{-2} S/cm for 0.6 AgI–0.4 $AgPO_3$ [12]. Without application of a dc bias voltage, the small capacitance of the tip/sample contact leads to impedance spectra below 1 MHz, which are entirely governed by electrode polarization. To

overcome this problem, we applied a negative bias voltage to the tip, thereby short-circuiting the double layer capacitance at the tip/glass interface by faradaic silver deposition. When the overpotential for silver reduction is sufficiently high, the polarization resistance should become small and the measured current should be determined by the spreading resistance R_{spread} due to migration in the glasses [13]. The deposited silver particles act themselves as nanoelectrodes, and the spreading resistance R_{spread} is related to the local nanoscopic conductivity σ_{nano} via:

$$R_{spread} = \frac{1}{4 \times r \times \sigma_{nano}} \tag{1}$$

with r denoting the radius of the deposited silver particle. For three different glasses with different macroscopic conductivity, we found good agreement between the macroscopic conductivity and the nanoscopic conductivity obtained from Eq. (1).

For local electrode applications, the shape of the *in-situ* deposited silver arrays on silver-ion-conducting solid electrolytes is of great concern. Peppler et al. [14] reported a solid-state electrochemical method for the growth of silver nanowires with controlled diameters using porous silicon templates. Rohnke and coworkers [15] demonstrated the cathodic deposition of silver whiskers acting as silver microwires in an Ag/AgBr/Ag arrangement. They were able to control the growth rate and the diameter of the microwires by current variation. Spangenberg et al. [16] reported the cathodic silver deposition in mechanically produced tracks on AgCl crystals using microelectrodes. They assumed that the higher surface energy in such tracks accompanied with an increased nucleation rate favors silver deposition in scratches.

In this paper, we systematically investigate the deposition of silver and lithium structures acting as electrodes. To this end, we carried out chronoamperometric measurements at different dc bias voltages on two highly conductive silver ion conducting phosphate glasses and on the LIC-GC. We compare the nanoscopic conductivity obtained at different dc bias voltages by means of Eq. (1) to the macroscopic conductivity of the sample. For the silver ion conductors, we show that deposited silver particles work perfectly as local electrodes even at low bias voltages. In contrast, we find large deviations of almost two orders of magnitude between the nanoscopic and macroscopic conductivity for the LIC-GC at low and moderate dc bias voltages. We suggest that this effect is caused by the existence of a resistive layer between the lithium particle and the LIC-GC surface.

Furthermore, we report on the modification of the silver glass surface with a laser micro-machining system in order to obtain silver band-like structures for local- or microband electrode application [17–19]. Metal doped glasses are suitable materials for the fabrication of microstructures over a large area by laser light [20]. Structuring of surfaces using a laser micro-machining system has two significant advantages in comparison to mechanical scratching techniques [16]: (1) Rapid free form design and ad-hoc implementation can be achieved very rapidly. (2) The laser itself acts as non-contact machining and "on-the-fly" processing on large areas. We have fabricated well-defined tracks with a width of 1 µm by laser ablation. Metallic silver was then deposited with a negatively charged AFM tip from one point along the border of the tracks, and thereby band-like silver structures were obtained. The current response was a direct measure of the deposition rate of silver atoms.

2. Experimental

Silver phosphate glass samples of composition (mol%) 20 AgI–80 AgPO$_3$ (glass I-20) and 40 AgI–60 AgPO$_3$ (glass I-40) were prepared as described in Ref [11]. The thickness of the glass sample was approximately 1 mm. The Ohara LIC-GC with a thickness of 150 µm is commercially available. For the AFM measurements, samples with an area of about 1 cm^2 were used. The nanoscopic measurements were performed under ambient conditions using a *NT-MDT-Solver P47* atomic force microscope with a conductive tip acting as working electrode. In the setup, an ion-blocking platinum layer is the large-area counter electrode, and the top contact is a conductive AFM tip. The main potential drop is concentrated at the AFM tip, so that a third reference electrode is not needed. To obtain reproducible results, the usage of cantilevers with high spring constants in the range of 40 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 1–2 µN. For the chronoamperometric measurements, the AFM was connected to a Novocontrol Alpha-AK impedance analyser equipped with a POT/GAL 15 V/10 A electrochemical interface.

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 30×30 or 40×40 µm^2. The topographical pictures were analyzed 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.

A New Wave Research QuikLaze 50 laser machining system was used for microstructure generation at the surface of the I-40 glass. The q-switched Nd:YAG solid state laser provides three wavelengths including 1064 nm, 532 nm and 355 nm. Feature sizes down to 1 µm were obtained on AgI-glasses using 532 nm pulses at a repetition rate of 50 Hz and a pulse width of 6 ns. The beam was focused by a Mitutoyo M Plan Apo NUV 50× objective lens (working distance 15 mm, NA = 0.42) and formed to the desired feature size by an adjustable aperture stop. Best results were obtained by overlapping 3-shot ablations at 0.3 GW/cm^2.

Field emission scanning electron microscopy (SEM) images and backscattered scanning electron microscopy (BSE) images were obtained using a JSM-7500F electron microscope (JEOL, Japan) equipped with a YAG-BSE detector (Autrata, Czech Republic).

3. Results and discussion

In order to probe the deposition of metallic particles, chronoamperometric measurements were combined with topographic imaging. When a critical cathodic voltage is applied to the conductive AFM tip, metal ions are locally extracted from the electrolyte and the current response can be attributed to metallic silver deposition. We have no indication for a decomposition of the glass due to silver reduction, although a platinum counter electrode was used. This is understandable, since the overall charge flow during the experiments is so small (in the range of 10^{-7} C) that the silver depletion in the double layer at the Pt counter electrode causes potential drops around 10 mV.

In Fig. 1a, a silver particle formed on the I-40 glass after applying a voltage pulse of −0.6 V for 1 s, is shown as an example. The silver particle exhibits a circular shape with dendritic structure. At different positions on the I-40 glass surface, particles with diameters between 3 µm and 25 µm and 1 to 1.5 µm in height were posited. In Fig. 1b, a deposited lithium particle on the LIC-GC is shown. In contrast to the silver particles, the lithium particles exhibit a compact structure.

In Fig. 2a, chronoamperometric measurements on the I-20 glass are exemplarily shown for three different dc bias voltages. When a critical dc bias voltage is exceeded, the current response can be attributed to silver deposition. The current I shows a power-law increase with time t: $I \propto t^{\alpha}$, with the exponent α being in the range of 0.7–0.85. In contrast, we obtained an exponent $\alpha \approx 0.5$ for lithium metal deposition (Fig. 2b) at all applied dc voltages, in agreement with our results in Ref. [21]. This indicates differences in the growth kinetics of silver and lithium particles, which will be the subject of future investigations.

Due to the fact that the silver particle continually grows during a voltage pulse, the local electrode area has reached maximum size when the voltage pulse is switched off. The nanoscopic conductivity