

In situ atomic force microscopy of the reduction of lead oxide nanocrystals immobilised on an electrode surface

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Abstract

Litharge (α -PbO) crystals with edge lengths between 100 and 500 nm have been deposited on polycrystalline gold electrodes and electrochemically reduced in one step to metallic lead. The reduction was followed by in situ atomic force microscopy. The results reveal that the reduction is an epitactic solid-state reaction with conservation of the initial crystal orientation. It was possible to depict the progressing of the reaction front supporting a simple theoretical model for the reaction mechanism. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The electrochemical transformation of one solid compound into another is a fascinating process about which there is still a lot to be learned. Electrochemical solid–solid transformations frequently occur in battery materials [1,2], and they are nowadays intensively studied with the technique of voltammetry of immobilised microparticles [3]. Some time ago we applied in situ X-ray diffraction to understand the reduction of litharge (α -PbO) crystals to metallic lead [4]. Within the time scale of the experiment a simultaneous decrease of the litharge signals and growing of the lead signals has been observed. Since the litharge crystals have been immobilised on a graphite electrode by pressing the electrode on a layer of litharge on a glass plate, all litharge crystals showed in X-ray diffraction a preferential orientation, which was completely retained during the reduction. This further supported the idea that the reduction is an epitactic solid-state transformation without any dissolved intermediates. The purpose of the present study was to get more detailed information on the course of this reaction by atomic force microscopy of single nanocrystals. Only this way it was expected that the

morphological change occurring upon reduction may become visible.

2. Experimental

2.1. Instrumentation

All measurements were made with an AFM/STM of Digital Instruments (Hardware: NanoScope Version 1.0, Software: NanoScope E Version 4.23r3) with its extern potentiostat Picostat™. A styropor box, pasted with an aluminium foil, acoustically shielded the microscope. A self-designed table served for vibration damping. For this purpose a large box filled with 200 kg sand was hanging on six springs in a frame. Two rubber stoppers on the bottom and on the top additionally dumped each table leg. The rubber stoppers were sandwiched between felt layers. The styropor box with the microscope was placed on a marble plate situated on a foam-rubber mat that was lying on the sand. With these precautions it was possible to work without any interferences, although the laboratory is situated on the third floor. All measurements were performed at room temperature in solution, which was thoroughly deaerated with nitrogen for at least 15 min.

Some electrochemical measurements were performed with the help of an AUTOLAB (EcoChemie, Netherlands).

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2.2. Chemicals

The α -lead oxide and the electrolytes KCl and KNO₃ (both p.a.) were from VEB Laborchemie (Apolda, Germany). The suspending liquid acetonitrile was manufactured by Merck (Darmstadt, Germany). The nitrogen gas was purchased from Messer Griesheim GmbH (Krefeld, Germany).

2.3. Electrodes

First experiments have been performed with highly oriented pyrolytic graphite electrodes (HOPG). With this substrate the performance of the STM/AFM instrument was tested and it could be shown that atomic resolution can be achieved. For electrochemical experiments the HOPG electrodes did not prove to be useful because it was not possible to obtain an even distribution of immobilised crystals on their surface. Due to the extreme smoothness and the high hydrophobicity of the HOPG surface, the PbO crystals formed heaps of conglomerates when the liquid in which they have been dispersed was slowly evaporated. Therefore gold electrodes were used, which have been fabricated by vapour deposition of gold on chromium covered quartz plates (Schröer GmbH, Lienen, Germany). The surface roughness of these electrodes is just sufficient to support the immobilization of well-separated PbO crystals, but not too large to conflict with the AFM measurements. The height of the gold hills is less than 10 nm compared to the level of the valleys.

A platinum wire served as pseudo reference electrode for the in situ AFM experiments. The potential of this electrode was relatively stable and 0.295 V vs. Ag/AgCl. All potentials given in this communication refer to the Ag/AgCl electrode (3 M KCl) with $E = 0.208$ V vs. SHE.

2.4. Immobilization of nanocrystals

To immobilize the nanocrystals a suspension of lead oxide in acetonitrile was used. The suspension was prepared as follows: 1 g α -PbO was suspended in 5 ml acetonitrile and after waiting 5 min, to allow most of the suspended crystals to sedimentate, some of the supernatant was sampled with a syringe. With the help of this syringe one drop (30 μ l) was placed on the gold surface. The suspending agent was slowly evaporated at room temperature within 6 h in a desiccator, the opening of which was closed by cotton. This way of immobilizing assured, that crystals with an average edge length of 300 nm were situated on the gold surface in a sufficient distance from each other. The crystals were absolutely stable sitting and could not be moved by the AFM tip.

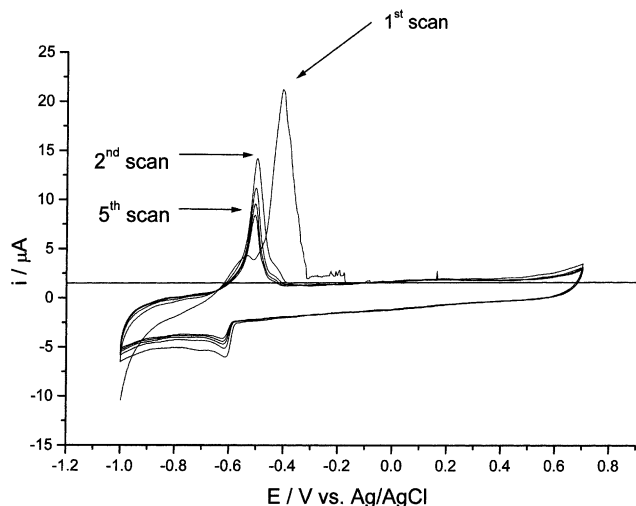
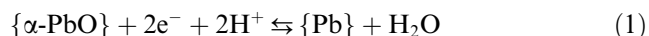


Fig. 1. Cyclic voltammograms of α -PbO crystals immobilised on a paraffin impregnated graphite electrode. The electrolyte solution contained 1 mol/l KCl, the scan rate was 50 mV/s.

3. Results

Fig. 1 depicts multiple cyclic voltammograms of α -PbO immobilised on a paraffin impregnated graphite electrode (PIGE). The voltammograms are within some millivolts identical with those recorded with the Pico-stat™ of the AFM microscope. Here we show the voltammograms with the PIGE measured with an AUTOLAB because of the superior resolution. At about -0.6 V vs. Ag/AgCl there is a reduction signal, and the oxidation signal occurs in the first cycle at a structured peak at about -0.4 to -0.3 V vs. Ag/AgCl. In all following cycles the oxidation of lead occurs at -0.5 V. The obvious reason for the shift of the oxidation peak is that the lead formed in the first reduction half-cycle results from the conversion of the solid lead oxide crystals to metallic lead according to the reaction:



(Braces denote solid phases). In the following cycles the lead is oxidised to dissolved lead ions (Pb^{2+}) and replated from solution. This can be seen in cyclic experiments also by AFM (see below) and this behaviour is well known from previous studies [5].

3.1. Single step reduction of α -PbO

Fig. 2(a) shows the atomic force micrograph of a lead oxide crystal located on the surface of a gold electrode. The α -PbO crystal has the typical shape of a tetragonal pyramid. Fig. 2(b) shows the lead crystal, which resulted after the α -PbO crystal was reduced according to Eq. (1) at -0.695 V vs. Ag/AgCl. Since

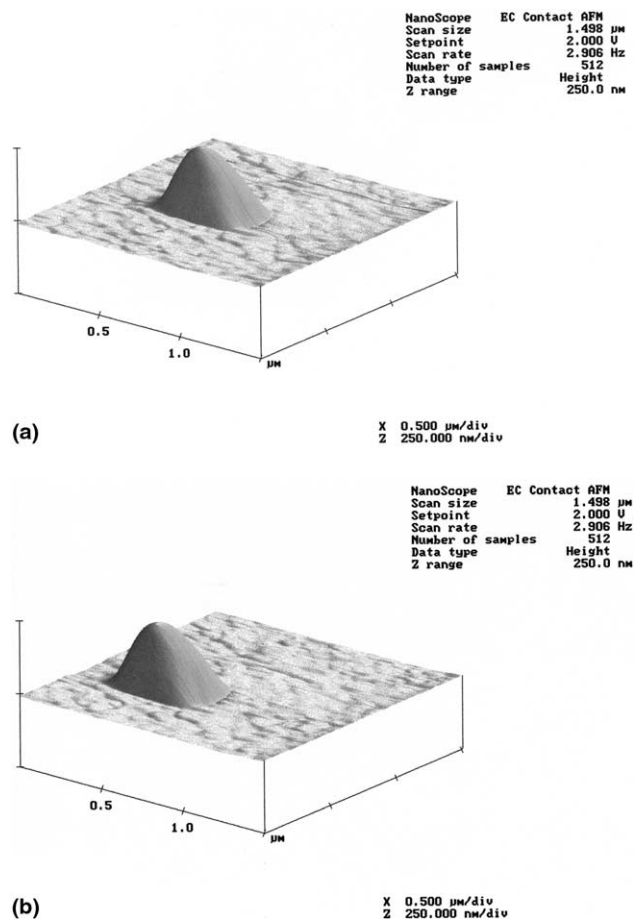


Fig. 2. (a) Atomic force micrograph of an α -PbO crystal on a gold surface in 1 M KCl electrolyte before the electrochemical reduction. (b) Atomic force micrograph of a Pb crystal formed by reduction of the α -PbO crystal shown in Fig. 2(a) (conditions same as Fig. 2(a)). The volume of this crystal is 21% less than that of the α -PbO crystal shown in Fig. 2(a).

the reduction was performed in one step, there was no chance to form dissolved lead ions in the course of transformation of α -PbO to metallic lead. From the micrograph data the volume loss was calculated to be 21%, in some other experiments between 16% and 19%. The calculation of crystal volumes was performed both manually after measuring the edge lengths of the crystal and also by integration with the computer software of the AFM microscope. The theoretical volume reduction from α -PbO to Pb is 23%. The small deviation between experimental and theoretical values may be due to the measuring procedure, i.e. a convolution by the tip. The tip radius was 10 nm, and hence the convolution of the crystal may have only a small influence on the results, bearing in mind the size and crystal angles of the studied crystals. Most importantly, Figs. 2(a) and (b) prove that the lead crystal is situated at exactly the same place at which there was the lead oxide crystal, and moreover, the crystal orientation remained the same as well. This is in full agreement

with the X-ray diffraction findings reported earlier [4], which have shown that the preferential orientation that the lead oxide crystals had on the electrode surface remained unchanged when they were reduced to lead crystals.

The next step was to get more information about the advancement of the reaction front during reduction. Therefore a short potential pulse into the potential range of reduction was applied. The electrode was initially at open circuit potential, stepped for 1 s to -0.695 V vs. Ag/AgCl, and finally stepped back to the open circuit potential to interrupt the reduction. Fig. 3(a) shows the lead oxide crystal before reduction, Fig. 3(b) shows the same crystal after a 1 s reduction, and Fig. 3(c), again the same crystal, after another reduction period of 1 s. Fig. 3(b) clearly shows a well-developed step at the reaction front and the volume shrinking from α -PbO to Pb (8% at the shown stage of reduction). This picture could be reproduced, provided that the reduction time was 1 s. Very interestingly, the reduction did not start at the entire three-phase junction gold – lead oxide – solution (the line surrounding the crystal at the bottom), but it was restricted to one crystal phase-gold-solution junction only! The reason for this result has to be studied in detail. One reason may be that the crystal adhered to the gold electrode only at that side, or that the nucleation for lead crystallization accidentally was fastest at that side. It is also possible that the epitactic growth of the lead crystal can only occur on one side of the lead oxide crystal. Fig. 3(b) shows a crystal of α -PbO, half of which is reduced to Pb. Clearly, there is no disintegration of the oxide crystal to an amorphous heap of lead but a smooth transition from one crystal into another, as it was already deduced from the in situ X-ray diffraction measurements. It can be speculated that it would be impossible to get the same picture when the crystal size is in the mm or cm range, because only in the sub-micrometer range the strains are sufficiently small to allow the compactness of such hybrid crystal of a parent and daughter compound. It is interesting to note that we could not yet freeze the half reduced state by interruption of the reduction. The reaction front proceeded further through the entire crystal, even when the electrode was finally disconnected from the counter electrode. A possible explanation could be that hydrogen was adsorbed at the gold surface during the partial reduction of the lead oxide crystal, and after disconnection of the electrodes a local element between the left-over lead oxide and the hydrogen loaded gold electrode prompted a reduction of the residual lead oxide. Another possibility is that the charge accumulated in the double layer of the gold electrode (roughly 10–20 μC) is responsible for the reduction of the tiny amounts of left-over lead oxide. From the density of PbO crystals on the electrode surface and their size the necessary charge is estimated

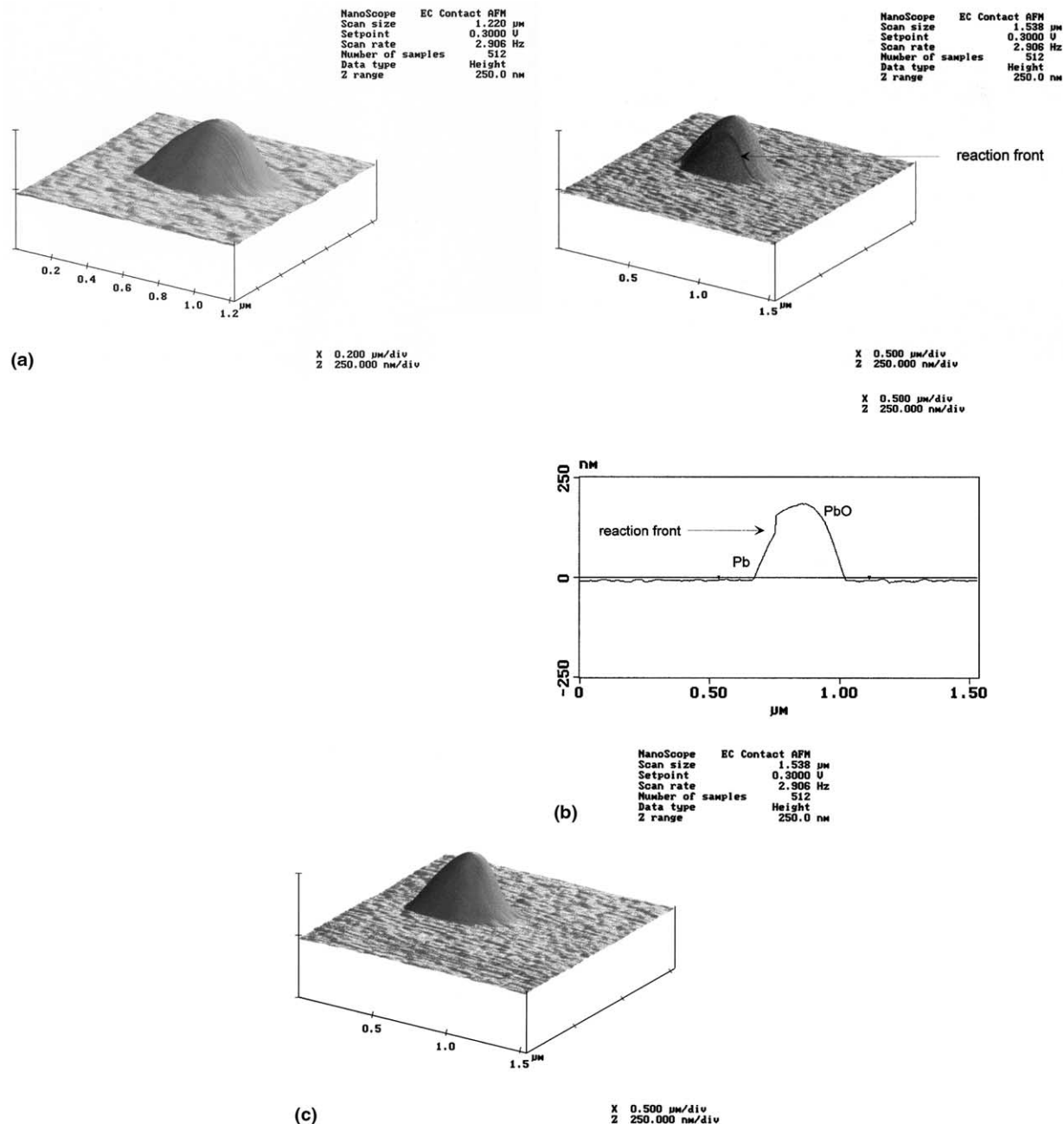


Fig. 3. (a) Atomic force micrograph of an α -PbO crystal on a gold surface in 1 M KCl electrolyte before the reduction (conditions same as Fig. 2(a)). (b) Atomic force micrograph of an α -PbO crystal on a gold surface in 1 M KCl electrolyte after a reduction for 1 s (Pb–PbO-hybrid) (conditions same as Fig. 2(a)). A step at the reaction front is clearly visible. The trace below the micrograph is a cut through the crystal perpendicular to the reaction front. (c) Atomic force micrograph of a Pb crystal after complete reduction of the α -PbO crystal shown in Figs. 3(a) and (b) (conditions same as Fig. 2(a)).

to be of the order 0.3–3 μC . This aspect has to be further studied in detail.

3.2. Cyclic reduction of α -PbO and Pb^{2+} , respectively

When a cyclic experiment is performed, i.e. first a reduction of $\{\alpha\text{-PbO}\}$ to $\{\text{Pb}\}$, followed by oxidation of $\{\text{Pb}\}$ to Pb^{2+} (dissolved), and replating of $\{\text{Pb}\}$ from

solution, this leads to the deposition of lead crystals in the neighbourhood of the initial Pb crystal (cf. Fig. 4). This observation supports the idea that in the second and following cycles of lead oxide reduction, the lead metal is deposited at *active centres* in the neighbourhood of the initially formed lead crystal. This further explains the cyclic voltammogram reported in Fig. 1, which is understandable assuming a smaller overpotential of

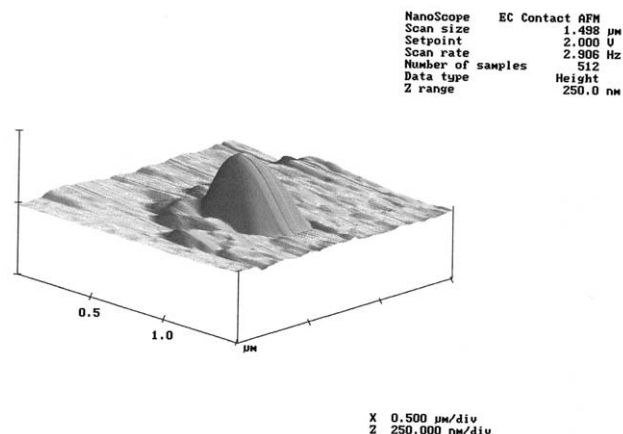


Fig. 4. Atomic force micrograph of a Pb crystal after complete reduction of an α -PbO crystal followed by one oxidation–reduction cycle. Lead deposits are clearly visible around the lead crystal in the middle (conditions same as Fig. 1(a)).

oxidation of lead deposited from solution compared to the oxidation of lead formed by direct transformation of the solid α -PbO crystal to a lead crystal.

4. Discussion

Atomic force microscopy gives evidence that the transformation of lead oxide nanocrystals into metallic lead crystals occurs without a morphological disintegration but as a process in which the initial crystal is continuously shrunk and reconstructed into the metal crystal. The orientation of the lead oxide crystal on the gold electrode is completely retained. Thus the AFM results fully confirm the earlier findings by in situ X-ray diffraction. Now it is possible to formulate a model, which explains the transformation of α -PbO into Pb on an atomic scale. With the X-ray results only there was still the possibility that the α -PbO crystals disintegrate upon reduction first to a small heap of amorphous lead that quickly (at least at the time scale of the X-ray diffraction measurements) recrystallizes to a lead crystal. Now with the AFM results a more precise picture can be drawn. Since the reduction of the nanosized lead oxide crystals occurs within 2 s (200–400 nm crystals) it is impossible to explain the reaction by lead ion or oxide ion diffusion within the lead oxide. The ionic conductivity of lead oxide at room temperature is practically zero [6]. Therefore a possible explanation is that the reduction occurs as an electron flux from the gold electrode into the lead oxide crystal simultaneous with a proton flux from the solution into the lead oxide (cf. Fig. 5). As a result of these two fluxes a reaction layer must form, which contains lead atoms and lead ions together with hydroxide ions and water molecules. This reaction layer may have a rather soft consistency allowing quick

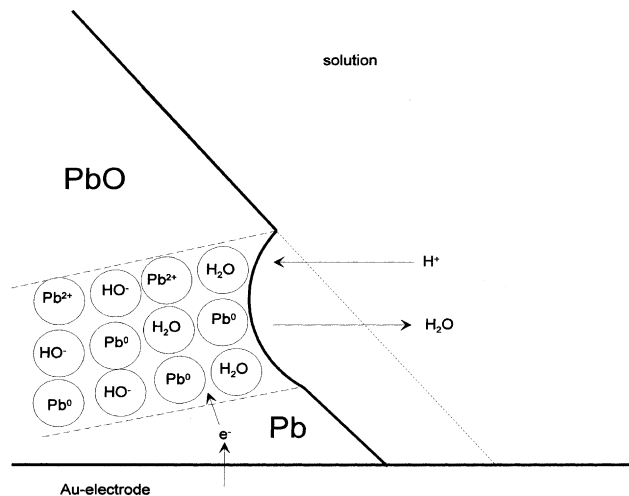


Fig. 5. Schematic model for the reduction process of an α -PbO crystal.

movement of the lead atoms towards the growing lead crystal interface. It can be regarded as a diffuse heterophase interface [7]. This model resembles that one for electrochemical oxidation of white phosphorus at a three-phase junction [8], and the electrochemical conversion of metal hexacyanoferrates [9]. It is also in line with theoretical models for the advancement of solid-state electrochemical reactions [10–12].

5. Conclusions

The reported in situ AFM studies of the electrochemical reduction of α -PbO show that the reaction is conservative with respect to the orientation of the starting crystals on the electrode surface. For the first time it was possible to make visible the progressing of the reaction through the crystal. As intermediates partially reduced lead oxide crystals could be detected, which obviously have an interface between the PbO and Pb domain. It will be interesting to see whether such partially reduced lead oxide crystals can be used as diodes because of their semiconductor–metal interface.

Acknowledgements

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