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Microelectrochemical lithography: A method for direct writing of surface oxides

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Abstract

An experimental set-up is presented that allows direct writing on a metal by local anodisation in a confined electrolyte volume. A scanning droplet cell with reference electrode and counter electrode is attached to an automated xyz stage and allows an efficient addressing of a small surface area. An automatic mode investigation of a material under systematic variation of formation parameters such as formation voltage, scan rate and potentiostatic or potentiodynamic formation mode is demonstrated. The influence of these parameters on the oxide film thickness and film properties are discussed. An example for the method of direct electrochemical oxide spot writing is given. The set-up can also be used in a manual mode to address a surface area of interest such as a pit, single grain, grain boundary or intermetallic inclusion.
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1. Introduction

Direct writing onto a metal by means of local anodic oxide formation can be performed by means of a laser in air [1] or in an electrolyte [2]. However, the oxide that forms will be heavily influenced by the high surface temperatures resulting in a completely different structure and thus different properties. Local anodisation can be performed after spin coating of a lacquer subsequent laser irradiation and development to expose small spots or lines to the electrolyte in which the oxidation can be performed [3]. But this method does not allow direct writing and in some cases the required use of aggressive chemicals such as potassium hydroxide solution gives rise to further limitations. Another approach for a local anodisation employs a small electrolyte droplet being held by the tip of a capillary [4]. The entire reference electrode and counter electrode system is mounted into that capillary to allow all common electrochemical methods to be performed [5,6]. The droplets are small enough to study electrochemical properties on single grains of gold [7], iron [8] and steel [9] or to study the influence of oxide formation conditions on a single grain of polycrystalline material such as titanium [10]. Since the localisation is in the micrometer range but the oxide film thickness is in the nanometer range, the local oxide formation does not differ from that on macroscopic samples. Still, a thermally activated field assisted ion movement is the rate determining step. From the diameter and the thickness of the oxide spot it is obvious that solely the field strength normal to the surface is relevant.

Parameters for the growth of oxide films on titanium have been recognised to be of significant importance for the properties of the films formed [11]. Armstrong and Quinn obtained lower titanium oxides at potentials <2 V [12]. Pesant and Vennereau proposed a complex mixture with hydrated oxides forming initially on titanium [13]. A systematic study on the influence of the field strength and the film thickness on the photoelectrochemical behaviour was performed by Schultze et al. [14]. Ohtsuka et al. found an influence of the growth rate on the optical properties [15] and on the semiconducting properties [16]. A microelectrochemical study was performed on a single grain of titanium in which different ratios between virtually defect free potentiostatic oxide and defect rich potentiodynamic oxide were formed. The reactivity of these sandwich oxides was monitored by means of a scanning electrochemical microscope and it was found that the reactivity increased

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with increasing amount of potentiodynamically formed oxide [10].

In all these studies the same trend was observed: the higher the scan rate during oxide growth was, the higher was the donor density correlating to a high number of defects left in the oxide. In metal insulator metal systems in which an anodic valve metal oxide film is employed as insulator an investigation of the oxide without an oxygen source becomes possible [17]. It could be demonstrated that after careful preparation the breakdown field strength was identical with the former oxide formation field strength for all valve metal investigated (aluminium, hafnium, niobium, tantalum and zirconium) except for titanium which displayed a lower stability with a breakdown field strength of $0.37\,GV\,m^{-1}$ [18]. To which extent these deviations must be ascribed to structural changes and whether or not they can also be removed by an electrical annealing like in the case of aluminium [19] will be the topic of another study.

In this study the feasibility of an efficient direct writing by means of local oxide formation will be demonstrated that allows a systematic formation of oxides under variation of parameters such as growth rate, thickness and formation condition (potentiostatic, potentiodynamic) on a small scale.

2. Experiments and results

2.1. Sample preparation

Titanium films 150 nm thick deposited on silica substrates (Marienfeld microscope cover glasses) were used as templates for the direct writing of the surface oxide by means of electrochemical oxidation. The silica substrates were cleaned using isopropanol and de-ionised water. The Ti thin films were deposited using an electron beam evaporation system having a base pressure of $10^{-4}\,Pa$ and their thickness was monitored in-situ using a quartz crystal micro-balance.

2.2. Electrochemical cell description

The anodisation of the Ti was achieved using the microelectrochemical cell schematically presented in Fig. 1 with acetate buffer electrolyte (pH 6.0) prepared from p.a. chemicals and de-ionised water. The body of the cell is represented by an acrylic block (20 mm × 20 mm × 10 mm) in which four connected channels (3.5 mm in diameter) were drilled. Each of the four channels can be sealed using a plastic screw. The reference electrode (RE) used was a capillary μ-AuHg/Hg$_2$(CH$_3$COO)$_2$/NaCH$_3$COO reference electrode having a 1 mm outer diameter and a 100 μm tip diameter. Details regarding its fabrication can be found elsewhere [6]. The RE was mounted through one of the screws fixing it to the body of the cell in a simple manner. The counter electrode (CE) was a high purity (99.999%) gold wire 200 μm in diameter mounted in a second screw. For maximising its surface, the inner cell part of the CE was mechanically flattened to a 1 mm wide band and was wrapped around the RE capillary as shown in the magnified part of Fig. 1. In a third screw, a 2.5 mm outer diameter and 1.5 mm inner diameter capillary was mounted representing
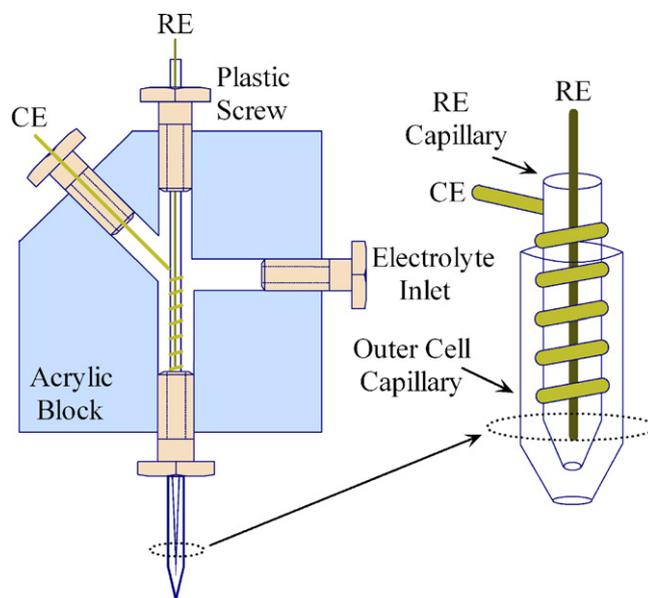

Fig. 1. Schematic of the microelectrochemical cell.

the electrolyte outlet of the cell. The capillary was previously pulled using a capillary puller (PC-10, Narishige) and tips ranging from 30 to 200 μm in diameter could be obtained using a micro-grinder (EG-400, Narishige). The lengths of the RE and CE were chosen in such a way that the tip of the RE capillary will be placed inside the outlet capillary, in proximity of its tip. The fourth screw was used for the mounting of the electrolyte inlet.

2.3. Hardware description

For pushing the electrolyte out of the cell, a computer controlled micro-syringe pump (Micro 4, World Precision Instruments) combined with a 100 μl syringe was used. With a resolution of 1 nl, small droplets of electrolyte were formed for contacting the working electrode (WE) represented by the Ti thin film. The electrical contacting of the WE was achieved using a tungsten needle pressed against the sample. The microelectrochemical cell was mounted on a 3D translation stage actuated by three computer controlled DC-mikes (C-862 Mercury) allowing the movement of the cell tip across the sample with a precision of 500 nm. Two video cameras are providing live video feedback from the top, for observing the sample, and from grazing incidence view, for observing the height of the cell tip above the sample. A potentiostat (Solartron Schlumberger 1287) was used for the anodisation of the Ti films and a lock-in amplifier (EG&G 7265) was used for superimposing a small AC perturbation on the cell and for monitoring the cell response.

2.4. Software

The control of the entire system was done using LabView® programming. The in house developed software allows the user to choose between manual or automatic operation of the direct writing system.
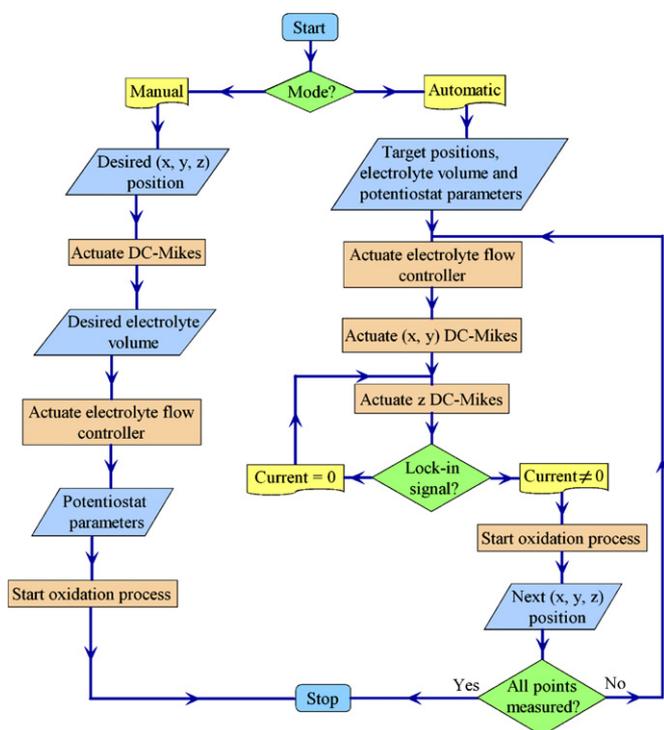
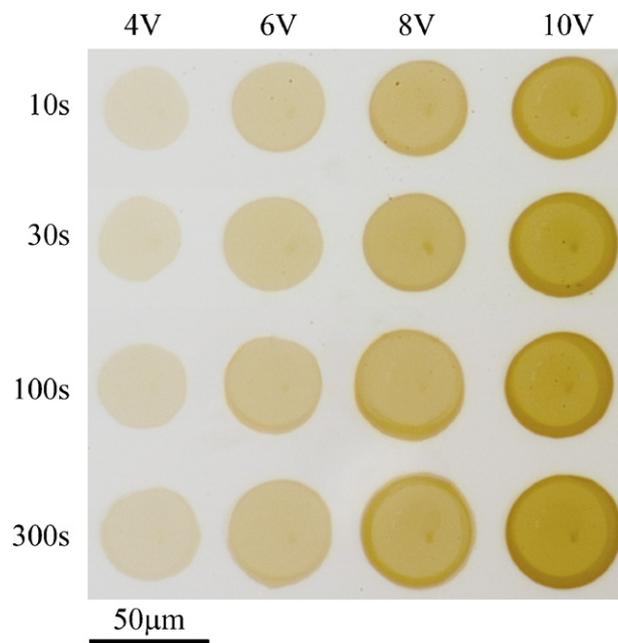Fig. 2. Block diagram of the direct writing system program.

Fig. 3. Optical micrograph of a matrix of oxide spots formed potentiostatically under variation of time and potential. The potential values are reported to SHE potential.

In the manual mode the user can move the cell tip to the desired location (x, y directions) by means of a drag and drop function and can approach the sample (z direction) using the right-click mouse button. The micro-syringe can be used for pumping a desired volume of electrolyte and using the video feed-back, the moment of the droplet contacting the surface can be visualised. The potentiostat can be controlled for the writing process and different parameters can be defined.

In the automatic mode, the user defines all the target points to be accessed, using the video feed-back, as well as the parameters for syringe controller and potentiostat and the software will handle the entire process automatically. Fig. 2 shows a block diagram of this system. First, the operating mode is selected in the software. In case of the manual mode, the operation is straightforward. After entering the desired coordinates in a user dialog, this information is immediately used to actuate the DC-mikes for addressing the position of interest. The desired electrolyte, also entered in a user dialog, will allow the electrolyte volume controller to dose the requested amount of liquid. Finally, the parameters for the potentiostat such as potential and time for a potentiostatic oxidation or the start, end and reverse potentials as well as the scan rate are feed in and the oxidation can be started. For the automatic mode on the other hand, the operation needs to be more sophisticated. The most sensitive aspect of the automatic handling of a 3D movement of the cell tip is the approach to the sample. This is realised using a proportional control with feed-back from the lock-in amplifier. A small perturbation voltage (10 mV, 1013 Hz) is superimposed on the DC signal from the potentiostat that will have a current oscillation with the same frequency through the WE only when the electrolyte droplet contacts the sample surface. The lock-in amplifier

locks on this frequency and monitors the current. Following this idea, a feed-back loop controls the approaching of the sample in small user-definable steps. Once the contact is achieved, the software continues the sequence by controlling the potentiostat for the oxidation and then moving to the next target point.

3. Application and discussion

Using the described method for direct writing, oxide dots were patterned on Ti films for analysing them as a function of different oxide growth parameters. Fig. 3 shows an optical microscope image of a matrix of oxide dots obtained potentiostatically for different anodisation time intervals. With increasing the potential, the thickness of the oxide increases and
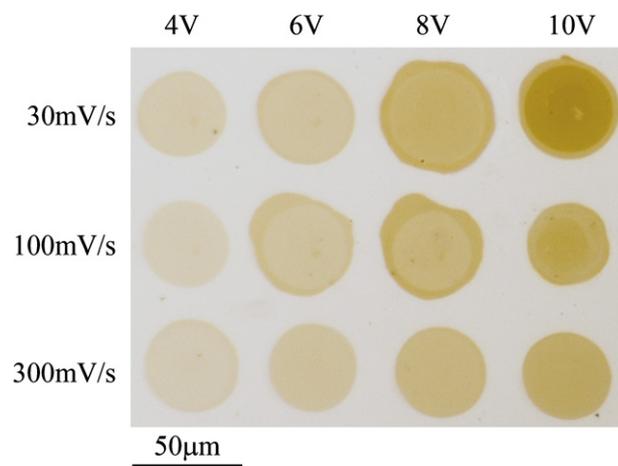

Fig. 4. Optical micrograph of a matrix of oxide spots formed potentiodynamically under variation of the scan rate and the formation potential. The potential values are reported to SHE potential.
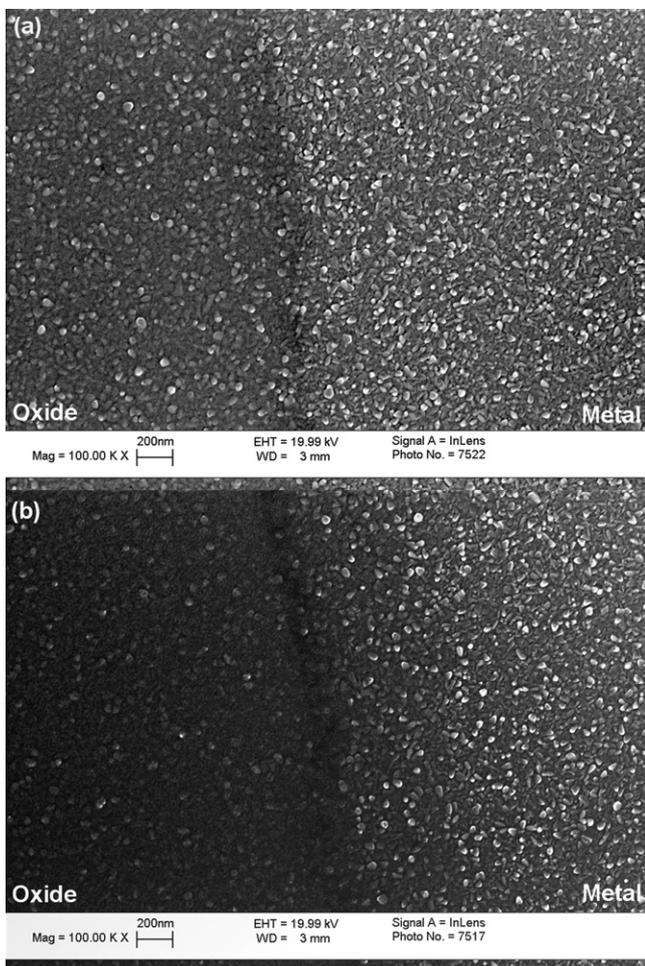
Fig. 5. SEM images of the edge of oxide dots grown potentiostatically on Ti thin films at (a) 5 V and (b) 10 V for 100 s.

causes a delayed oxide growth which can in fact be recognised in Fig. 3. Moreover, this is directly seen from an inspection of the oxide spots formed. A darker rim around the inner circle is found at higher oxidation potentials and longer anodisation times.

Fig. 4 shows an optical microscope image of a matrix of oxide dots anodised potentiodynamically with different scanning rates of 30, 100 or 300 mV s^{-1} up to various end potentials of 4, 6, 8 or 10 V. During the anodisation using these scan rates, current densities of 130, 400 and 1200 µA cm^{-2}, respectively, were measured indicating an oxide formation factor of 2.4 nm V^{-1}. As expected, the oxide appears darker with increasing the final anodisation potential. There is also a significant influence of the scan rates which is best seen for the 10 V scans in which the slowest scan rate of 30 mV s^{-1} yields the darkest oxide. The same tendency is found for all anodisation potentials, demonstrating that a significant retardation of the oxide formation is found also for the potentiodynamic oxide formation. A comparison of the shape of the oxide dots formed shows the strongest dependency for the slowest scan rate. In other words, at a slow scan rate the shape is more susceptible to disturbing effects whereas the shape is quite stable at a scan rate of 300 mV s^{-1}.

The microstructure of the Ti thin film as well as the transition region between the oxide and the metal at the edge of the oxide dots can be observed in the SEM images of Fig. 5. In part (a) of the Fig. 5 the boundary of an oxide dot is presented that was grown potentiostatically at 5 V for 100 s, and in part (b) the boundary of a dot grown potentiostatically at 10 V for 100 s is shown. When analysing the two images, a few observations can be made. First, the Ti film surface is compact with a grain size of around 50 nm. The oxide can be observed indirectly in the left side of the images from the Ti grains being less visible with increasing anodisation voltage, suggesting the thickness depen-

as a result the contrast between the dots and the background becomes more pronounced. For a given potential, the contrast of the dots increases slightly with time. This indicates that there is only a marginal increase in film thickness. These findings are in agreement with the high-field model of oxide growth which assigns a constant anodisation charge to each decade in time for a potentiostatic experiment [20]. For the low voltage anodisation the typical capacity of the oxide is between 30 and 50 µF cm^{-2} [14]. The increase in oxide thickness starts after about 100 µs to 1 ms, depending on the field strength applied; 4–5 decades in time are already covered after 10 s. The longest time investigated here was 300 s corresponding to an additional 1.5 decades in time as compared to the shortest anodisation time and thus a maximum increase of the oxide by about 30%.

The diameter of the dots is increasing for both parameters, the applied potential and the anodisation time. Whereas the influence of the applied voltage on the diameter increase was expected for the electrocapillarity following the Lippmann equation, the influence of the anodisation duration is attributed to another effect. The surface of the working electrode underneath the rim of the capillary forms a confined zone. This is coupled to the counter electrode through a very thin and thus high ohmic electrolyte film. The potential drop within this electrolyte film
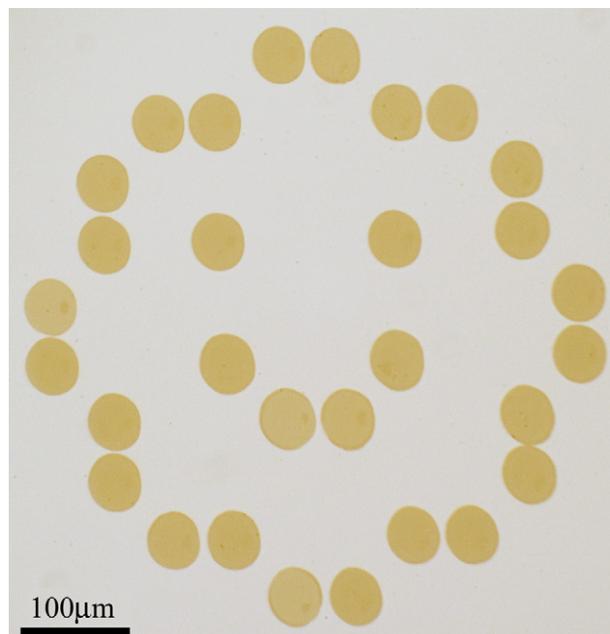

Fig. 6. Oxide dots patterned on Ti thin films using potentiostatic anodisation at 8 V (SHE).

dence on the applied voltage. The oxide/metal boundary is very sharp, the transition being completed after around 400 nm in the case of thicker Ti oxide in the part (b) of Fig. 5. This demonstrates that transient instabilities of the drop size and potential dependent effects do not exceed this range, resulting in an estimated error of the area of less than 1%.

An example of the direct writing of surface oxides is given in Fig. 6. This optical microscope image shows an arrangement of oxide dots on the Ti thin film with a location previously defined in the software. The dots were obtained using a potentiostatic anodisation at 8 V (SHE) for 10 s. The charge consumed for the anodisation of one single dot up to 8 V was 890 nC. The homogeneous diameter of spots achieved here proves that the use of a sealant at the tip of the capillary is not always necessary for achieving circular spots. For other experiments however, the use of a soft plastic capillary [21] or a sealant at the tip of the glass capillary [22] can be advantageous.

4. Conclusions

A method for direct writing of surface oxides and its application in microelectrochemical lithography is presented. Local anodisations in a confined electrolyte volume on evaporated Ti film is possible using a computer assisted set-up actuating a droplet cell which can be operated in a user-friendly environment in either manual or automatic mode. Potentiodynamically and potentiostatically grown oxide dots with a diameter of 30 μm were analysed as a function of the rate of voltage increase and anodisation time, respectively. The shape modifications and the optical microscope contrast of the oxide dots written were discussed. Transition regions at the edge of oxide dots of maximum 400 nm could be observed suggesting that a sharp boundary between the oxide and metal can be obtained even with a free hanging droplet that would avoid side effects such as crevice corrosion underneath a sealing.

Acknowledgement

References

[1] R.J. von Gutfeld, J. Opt. Soc. Am. B 4 (1987) 272.
[2] K. Bade, O. Karstens, A. Michaelis, J.W. Schultze, Faraday Discuss. 94 (1992) 45.
[3] M. Schweinsberg, S. Kudelka, A. Michaelis, J.W. Schultze, Mater. Corros. 49 (1998) 161.
[4] A.W. Hassel, M.M. Lohrengel, Electrochim. Acta 42 (1997) 3327.
[5] A.W. Hassel, K. Fushimi, M. Seo, Electrochem. Comm. 1 (1999) 180.
[6] K.A. Lill, A.W. Hassel, J. Solid State Electrochem. 10 (2006) 941.
[7] A.W. Hassel, M. Seo, Electrochim. Acta 44 (1999) 3769.
[8] A. Schreiber, J.W. Schultze, M.M. Lohrengel, F. Kármán, E. Kálmán, Electrochim. Acta 51 (2006) 2625.
[9] K.A. Lill, A.W. Hassel, G. Frommeyer, M. Stratmann, Electrochim. Acta 51 (2005) 978.
[10] A.W. Hassel, K. Fushimi, T. Okawa, M. Seo, Local analysis of anodic oxide films on titanium by scanning droplet cell and scanning electrochemical microscope, in: A.C. Hillier, M. Seo, S.R. Taylor (Eds.), Localized In Situ Methods for Investigating Electrochemical Interfaces, Electrochem. Soc. Proc. PV 99-28 (1999) 166.
[11] M. Stern, H. Wissenberg, J. Electrochem. Soc. 106 (1959) 755.
[12] N.R. Armstrong, P.K. Quinn, Surf. Sci. 67 (1977) 451.
[13] J.C. Pesant, P. Vennereau, J. Electroanal. Chem. 106 (1980) 103.
[14] J.W. Schultze, U. Stimming, J. Weise, Ber. Bunsenges. Phys. Chem. 86 (1982) 276.
[15] T. Ohtsuka, N. Nomura, Corros. Sci. 39 (1997) 1253.
[16] T. Ohtsuka, T. Otsuki, Corros. Sci. 40 (1998) 951.
[17] D. Diesing, A.W. Hassel, M.M. Lohrengel, Thin Solid Films 342 (1999) 282.
[18] A.W. Hassel, D. Diesing, Thin Solid Films 414 (2002) 296.
[19] A.W. Hassel, D. Diesing, Electrochem. Comm. 4 (2002) 1.
[20] M.M. Lohrengel, Mater. Sci. Eng. R11 (1993) 243.
[21] A.W. Hassel, Diploma thesis, Heinrich-Heine-Universität Düsseldorf, Germany, 1993.
[22] M.M. Lohrengel, A. Moehring, M. Pilaski, Electrochim. Acta 47 (2001) 137.