

Synthesis and characterization of catalyst layers for direct methanol fuel cell applications

M.-S. Löffler,^a B. Groß,^a H. Natter,^a R. Hempelmann,^{*a} Th. Krajewski^b and J. Divisek^c

^a Institut für Physikalische Chemie, Universität des Saarlandes, D-66123 Saarbrücken, Germany

^b Institut für Neue Materialien gem. GmbH, Universität des Saarlandes, D-66123 Saarbrücken, Germany

^c Institut für Werkstoffe und Verfahren der Energietechnik, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

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A preparation method for catalyst layers of platinum nanoparticles, as used in direct methanol fuel cells, based on pulsed electrochemical deposition within the three-phase boundary regions responsible for electrochemical reactions, was developed. A platinum precursor was brought into a carbon–Nafion layer and platinum was deposited *in situ* on the carbon surface. The size, size distribution and crystallinity of the deposited catalyst particles were determined by means of high-resolution transmission electron microscopy and X-ray diffraction measurements. The electrochemically active surface area of the deposited catalyst material was investigated by cyclic voltammetry, analysing the Pt–H oxidation peak.

Introduction

The search for efficient and inexpensive catalyst materials is a challenging problem for all proton-exchange-membrane fuel cells (PEMFC), especially for the direct methanol fuel cell (DMFC), where a relatively high catalyst loading is still required.¹ The problem is mainly caused by the high overpotential of the methanol oxidation on the fuel cell anode due to the poor reaction kinetics.² Platinum and other noble metals, which are typically used as catalysts in PEMFC electrodes, are one of the major factors for cell costs. In order to be commercially viable a distinct reduction in the catalyst loading in the DMFC is necessary.

The common preparation techniques for catalyst layers in fuel cell electrodes start from carbon black covered with platinum (pre-catalysation). But in this way only a low catalyst utilisation can be reached^{3,4} since a considerable fraction of the catalyst material is not in direct contact with the three-phase boundary consisting of proton-conducting electrolyte, electrode and fuel. McBreen³ has shown that without direct contact platinum particles have no catalytic effect and are unable to contribute to electrochemical reactions. Consequently a distinct reduction in the catalyst load can be realized by localizing the catalyst particles exclusively in the three-phase boundary regions, which is only possible *a posteriori*. Some methods of post-catalysation have been described in which platinum is deposited on a carbon–Nafion layer from an outer aqueous plating bath containing a platinum cation species.^{5–7} The disadvantage is that only the interface of the electrode layer is activated, not the layer in its full depth.

In this work we describe a new preparation method which avoids this disadvantage: A platinum precursor is brought into the carbon–Nafion layer, and platinum is electrochemically deposited site-selectively *in situ* on the carbon surface. A further advantage of this method is that catalyst layers can be prepared without expensive outer plating baths.

In order to achieve platinum deposition in the form of small nanoparticles, we applied rectangular current pulses as well as

constant current during the electrolysis. For several years pulsed electrodeposition (PED) has been used for the preparation of nanocrystalline metals and alloys, for instance nano-Ni,⁸ nano-Pd,⁹ nano-Fe¹⁰ or nano-Cu.¹¹ By reducing the crystallite size the electrochemically active platinum surface area can be increased.¹²

Theoretical

Pulsed electrodeposition

For the electrochemical deposition of metals with nanocrystalline microstructure, very small crystallites have to be formed at the cathode. The method is based on the electrochemical version of the Kelvin equation:¹³

$$r_c = \frac{2\gamma V_m}{ze_0|\eta|} \quad (1)$$

where r_c is the critical nucleation (grains with $r > r_c$ are stable), γ the specific surface energy, V_m the atomic volume in the crystal, z the number of elementary charges e_0 and η the overvoltage.

According to eqn. (1), the higher the overvoltage, the smaller the crystallites. With the high voltage, a high current is connected, leading to a very high deposition rate of the metal cations from the electrolyte. The control of this process *via* eqn. (1) is possible only for a few milliseconds; after that time the concentration of metal cations in the vicinity of the cathode is reduced so far that the process would become diffusion-controlled. Therefore, in order to maintain control of the grain size, one has to apply a pulsed current (we use rectangular pulses), with correspondingly short pulse widths (a few milliseconds). In the break between two pulses (several tens of milliseconds), metal cations diffuse, as desired, from the bulk of the electrolyte into the vicinity of the cathode, and the next pulse can be applied.

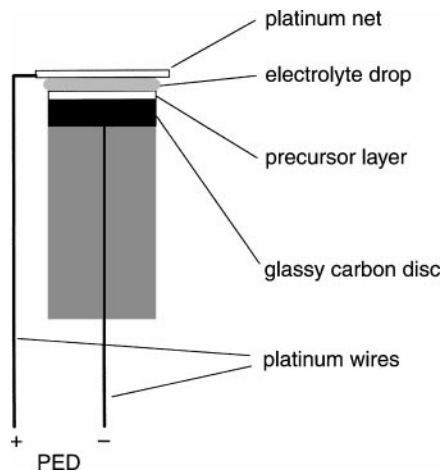


Fig. 1 Schematic set-up of the cell for platinum deposition in model electrodes.

Experimental

Electrode preparation

For our experiments we used model electrodes consisting of sprayed catalyst layers on glassy carbon substrates. For the preparation of the precursor layers a suspension of Nafion TM 117 solution in isopropanol and high-surface-area carbon (Vulcan XC72) was dispersed using an ultrasonic bath and an Ultraturrax homogenizer. The platinum precursor salt was dissolved in isopropanol and added to the suspension. The resulting solution was sprayed on glassy carbon discs of about 1 cm in diameter. The layers were dried in a furnace at ambient atmosphere in order to remove all remaining solvents. If the precursor layers are sprayed onto the glassy carbon discs in the state as purchased, the smooth surface impedes adhesion. Several adhesive agents (glycerol, acetyl-

Table 1 Cross-checking of the weighing results by ICP-OES measurements. The values correspond to the platinum contents before the platinum deposition

Sample	1	2	3	4	5
Pt content (weighing)/mg	0.49	0.44	0.41	0.38	0.53
Pt content (ICP-OES)/mg	0.55	0.51	0.44	0.40	0.60

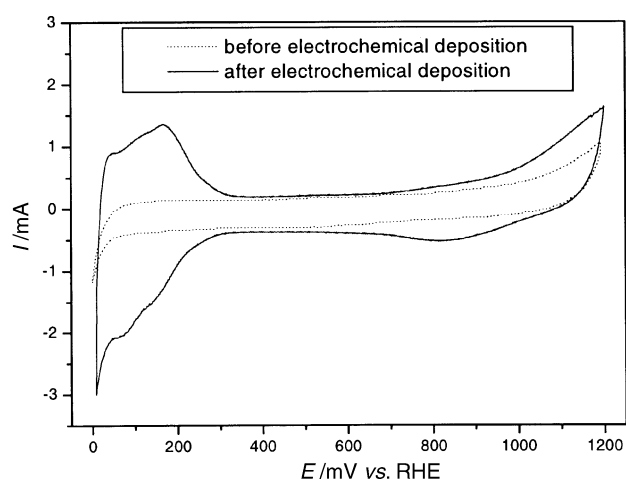


Fig. 2 CVs in 1M H₂SO₄ before and after electrochemical deposition using H₂[PtCl₆]·aq as platinum precursor. This CV is representative for hydrogen as fuel.

acetone and ethyl acetoacetate) were tested as a means to avoid this problem, but roughening the glassy carbon discs with emery paper in order to enlarge the surface area turned out to be the best way to get proper adhesion without any adhesive agent. Several platinum precursor salts were tested. The platinum content in the precursor layers (0.1–0.5 mg cm⁻²) was calculated by weighing the glassy carbon disc before and after spraying. The results from weighing five samples were cross-checked by inductively coupled plasma optical-emission spectroscopy (ICP-OES) measurements prior to the platinum deposition (Table 1). The precursor layers were between 10 and 20 μm thick. Platinum was electrochemically deposited on the carbon support, see Fig. 1. For PED a programmable pulse generator HAMEG HM 8130 was used to adjust the pulse width and pulse current density. A platinum net served as anode. Pulse width and pulse current density were monitored with a Tektronix TDS 210 oscilloscope.

High-resolution transmission electron microscopy (HR-TEM)

This was used in order to investigate size, size distribution and degree of agglomeration of the deposited platinum particles. The TEM samples were prepared by drying and pulverizing the carbon–Nafion layer. The powder was suspended in ethanol, deposited on a copper net and dried. For the measurements a Philips CM 200 FEG microscope attached to an Edax DX-4 X-ray spectrometer was used.

X-Ray diffraction (XRD)

The samples were also characterized by XRD measurements in order to verify the deposition of platinum and to check the crystallinity of the platinum particles. The crystallite size of the deposited particles could be estimated by evaluating the line width of the platinum[111] Bragg peak applying the Scherrer method. A Siemens D-500 diffractometer with Ni-filtered Cu-Kα radiation and a secondary pyrolytic graphite monochromator at room temperature was used. The measuring conditions for the model electrodes were scan steps of 0.02° with a scanning time of 8 s.

Cyclic voltammetry (CV)

The deposits were electrochemically characterized by CV employing a potentiostat EG&G INSTRUMENTS Modell 6310. This technique has proved to be quite valuable for evaluating the electrochemically active surface area of electrodes.¹⁴ A common electrochemical cell was used for the measurements in 1 M H₂SO₄ solution at room temperature. Highly purified nitrogen gas was bubbled through the solution prior to the measurements. The counter and the reference electrodes were a 1 cm² platinum net and a reversible hydrogen electrode (RHE), respectively. CVs were generally recorded at a scan rate of 20 mV s⁻¹. The charge of hydrogen oxidation can be obtained by integrating the CVs in the potential range from 0 to 0.3 V vs. RHE. This charge is representative of the electrochemically active surface area of the deposited platinum particles.

Results and discussion

Electrode preparation

As platinum precursor platinum(II) nitrate, Pt(NO₃)₂, hexachloroplatinic acid, (H₂[PtCl₆]·aq) and tetraammine platinum(II) chloride, ([Pt(NH₃)₄]Cl₂·H₂O), were tested. Using Pt(NO₃)₂ as platinum precursor the CVs of model electrodes already show catalytic platinum activity before the electrodeposition. Evidently the uncomplexed Pt(II) ion is already reduced, prior to the electrochemical deposition, by one of the components of the spray suspension. For that reason, platinum nitrate is not useful for this kind of prep-

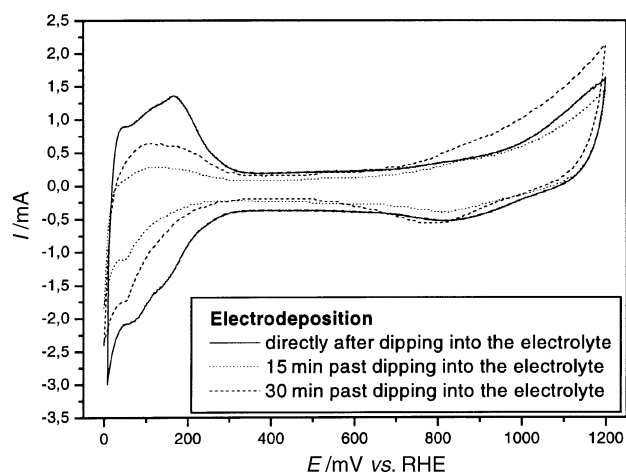


Fig. 3 Evidence for diffusion of $\text{H}_2[\text{PtCl}_6] \cdot \text{aq}$ out of the catalyst layer; deposition in 300 ml of 1M H_2SO_4 .

eration technique. Tetraammine platinum(II) chloride, ($[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$), is insoluble in the Nafion TM 117 solution; so in postcatalysation methods it can only be employed if an outer aqueous plating bath is used. As shown in Fig. 2 the electrode preparation with chloroplatinic acid, ($\text{H}_2[\text{PtCl}_6] \cdot \text{aq}$), as platinum precursor was successful and platinum could be deposited on the carbon substrate. The precursor layers should not be dried at temperatures above 50°C because of the thermal decomposition of $\text{H}_2[\text{PtCl}_6] \cdot \text{aq}$ forming insoluble PtCl_2 and eventually, at temperatures $>115^\circ\text{C}$, elemental platinum.¹⁵ $\text{H}_2[\text{PtCl}_6] \cdot \text{aq}$ partially dif-

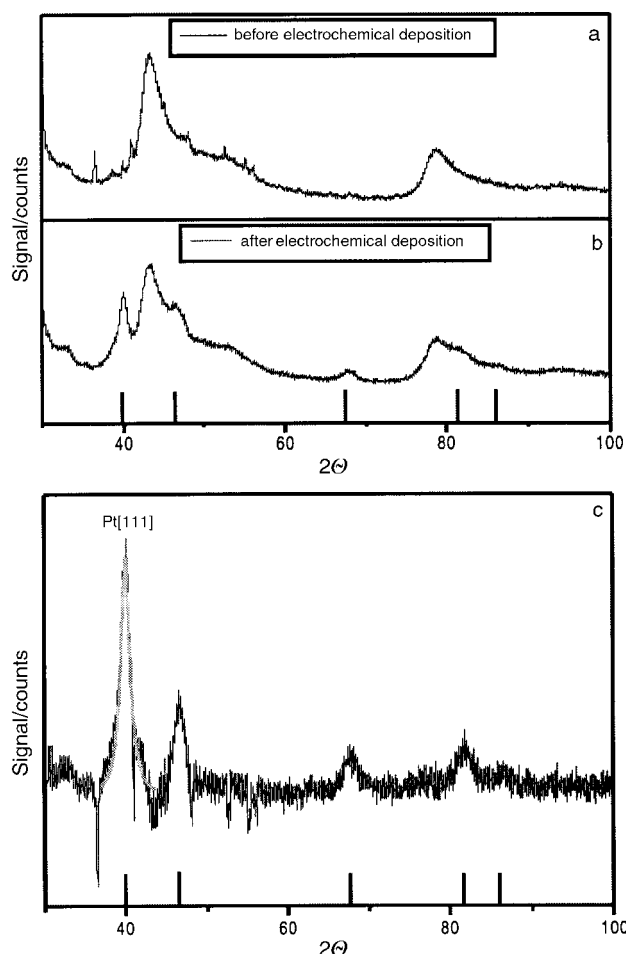


Fig. 4 a,b: XRD pattern of a model electrode before and after constant current deposition; c: The difference diffractogram shows the diffraction pattern of the platinum nanoparticles.

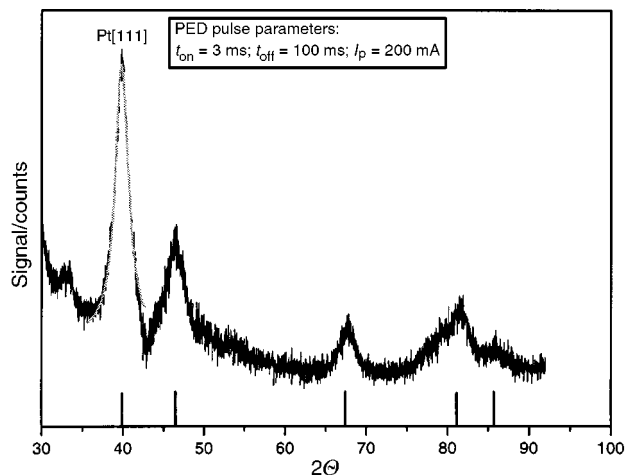


Fig. 5 Difference diffractogram of a model electrode after PED.

fuses out of the carbon-Nafion layer into the electrolyte during the deposition (Fig. 3). For that reason it is important to keep the volume of the electrolyte as low as possible (Fig. 1).

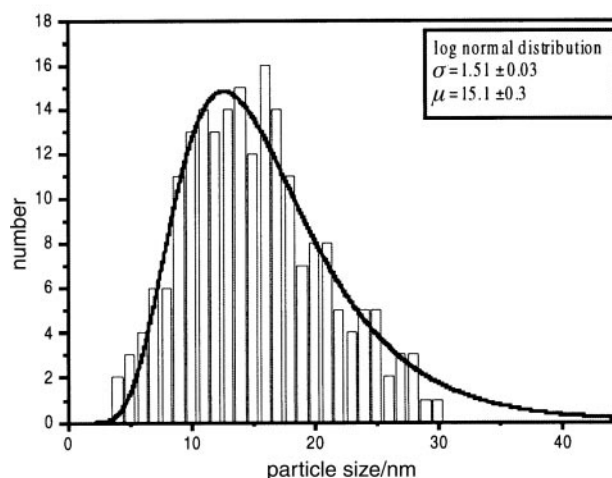
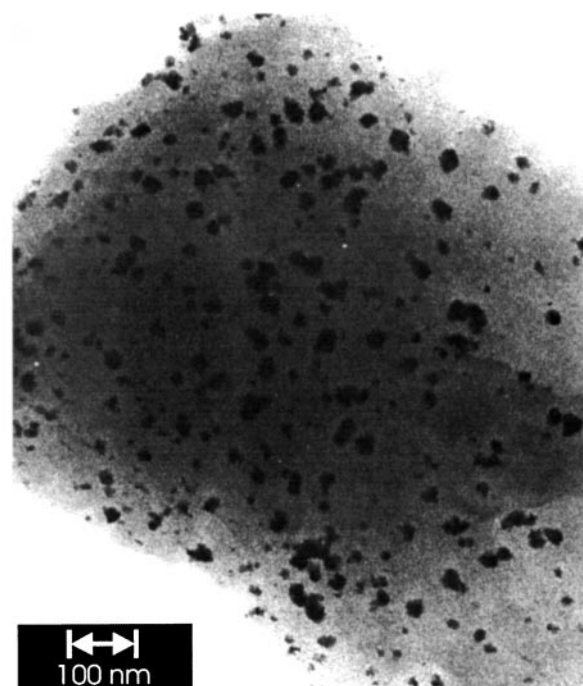


Fig. 6 Electron micrograph of a model electrode after constant current deposition and size distribution of the platinum particles.

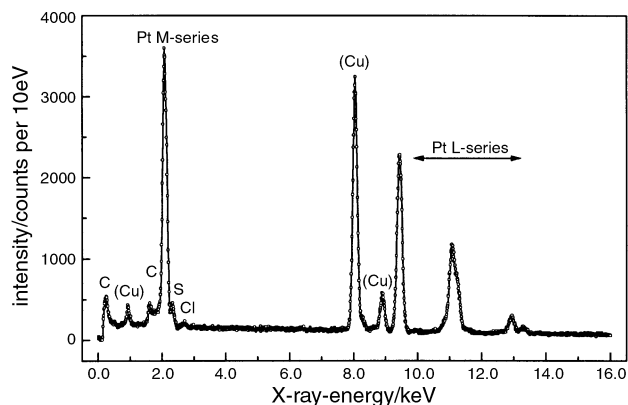


Fig. 7 EDX spectrum of a catalyst layer after platinum deposition.

Structural and electrochemical electrode characterization

The deposition of platinum in the precursor layers could be verified by recording X-ray diffractograms of a model electrode before and after PED as shown in Fig. 4. The peaks in Fig. 4(a) are due to reflexes of the glassy carbon disc and the hexachloroplatinic acid precursor. Subtracting the XRD patterns of Fig. 4a and Fig. 4b, the pure platinum diffractogram after constant current deposition is obtained (Fig. 4c); reflections with apparently negative intensity result from the platinum precursor before the platinum deposition (Fig. 4a). A fit of the Pt[111]-peak with a Lorentzian function and a subsequent Scherrer analysis yields a volume-weighted average grain size of about 9 nm after constant current deposition. As shown in Fig. 5 the pulsed electrodeposition results in a peak broadening of the Pt[111] reflex; consequently the Scherrer analysis yields a volume-weighted average grain size of about 6 nm.

Furthermore, the particle size and size distribution were analysed using HR-TEM. Fig. 6 shows an electron micrograph of a model electrode after the constant current deposition of platinum with the platinum particles represented as dark spots on the carbon support (gray background). An energy dispersive X-ray (EDX) spectrum of the catalyst layer proves the presence of platinum besides carbon, chloride and sulfur (Fig. 7). The copper peaks are due to the copper net carrier. The size histogram, evaluated by counting out two hundred particles, shows a maximum at about 12 nm. The data fit well to a log-normal distribution function (solid line), yielding a median size $\mu = 15.1$ nm, a geometrical standard deviation $\sigma = 1.51$ and thus a volume averaged size of 27.4 nm.

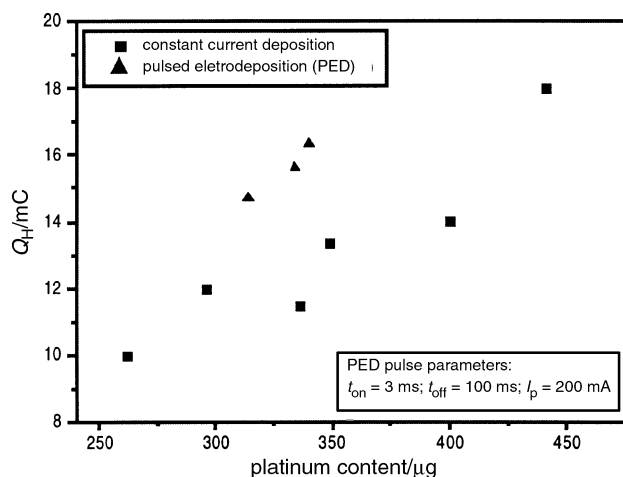


Fig. 8 Correlation between charge of hydrogen oxidation Q_H and the platinum content; Q_H was obtained by integrating the CVs in 1M H_2SO_4 in the potential range 0 to 0.3 V vs. RHE.

TEM images of the samples after PED show a high degree of agglomeration; thus it is difficult to determine the size distribution of these samples by analysing the TEM images.

The catalytic activity of the model electrodes was analysed using CV. Integrating the Pt-H oxidation peak, the charge of hydrogen oxidation Q_H could be obtained, which is representative of the electrochemically active surface area. The experiments were carried out for several precursor layers containing different platinum amounts. As shown in Fig. 8 Q_H increases linearly with the platinum content. PED of platinum obviously causes an increase in the electrochemically active surface area (triangles in Fig. 8).

Conclusion

Model electrodes with catalyst layers could be synthesized starting from a platinum salt as precursor in the carbon-Nafion layer. Several platinum salts were tested; hexachloroplatinic acid, $H_2[PtCl_6] \cdot aq$, turned out to be most suitable for this preparation technique. Platinum nanoparticles were prepared on the carbon surface by pulsed as well as constant current electrodeposition, site selectively at the three-phase boundary regions. The catalyst layers were structurally characterized by HR-TEM and XRD and electrochemically by CV. Both electron micrographs and XRD patterns verified the nanocrystalline shape of the platinum particles. First results show that an increase in catalytic activity is possible applying PED.

Further systematic investigations concerning the structure-property relationship between the size and shape of the platinum nanoparticles and electrocatalytic activity as well as the comparison of our preparation technique with other methods for the fabrication of membrane-electrode assemblies are in progress.

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References

- H. Wendt and M. Götz, *Chemie Unserer Zeit*, 1997, **6**, 301.
- Th. D. Jarvis and E. M. Stuve in *Electrocatalysis*, J. Lipkowski and P. Ross, Wiley-VCH, 1998, p. 109.
- J. McBreen, *J. Electrochem. Soc.*, 1985, **132**, 112.
- S. Srubivasab, O. A. Velev, A. Parthasarathy, D. J. Manko and A. J. Appleby, *NASA Conference Publication*, 1989, p. 3125.
- E. J. Taylor, E. B. Anderson and N. R. K. Vilambi, *J. Electrochem. Soc.*, 1992, **139**, L45.
- M. W. Verbrugge, *J. Electrochem. Soc.*, 1994, **141**, 46.
- J. Niebling and K. Gorgos, *US Pat.*, 5 084 144, 1992.
- H. Natter, M. Schmelzer and R. Hempelmann, *J. Mater. Res.*, 1998, **13**, 1186.
- H. Natter, T. Krajewski and R. Hempelmann, *Ber. Bunsen-Ges. Phys. Chem.*, 1996, **100**, 55.
- H. Natter, M. Schmelzer, M.-S. Löffler, C. E. Krill, A. Fitch and R. Hempelmann, *J. Phys. Chem.*, 2000, **104**, 2467.
- H. Natter and R. Hempelmann, *J. Phys. Chem.*, 1996, **100**, 19525.
- J. B. Goodenough, A. Hamnett, B. J. Kennedy, R. Manoharan and S. A. Weeks, *Electrochim. Acta*, 1990, **35**, 199.
- E. Budevski, G. Staikov and W. Lorenz, *Electrochemical Phase Transformation and Growth*, VCH, Weinheim, 1996.
- E. A. Ticianelli, C. R. Derouin, A. Redondo and S. Srinivasan, *J. Electrochem. Soc.*, 1988, **135**, 2200.
- Gmelins Handbook of Inorganic Chemistry*, Sys.-Nr., **68**, Part C, 79