Feature Article

Fabrication and Characterization of Needle-Type Pt-Disk Nanoelectrodes

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Abstract
Needle-type disk shaped Pt-microelectrodes have been fabricated by simultaneous pulling of a quartz-glass capillary and an inserted Pt-wire using a laser puller. After polishing, microelectrodes with sub-μm diameter were obtained with the smallest diameter as little as about 10 nm. These nanoelectrodes have been characterized by means of scanning electron microscopy (SEM), cyclic voltammetry in aqueous and organic electrolyte, and Z-approach curves in scanning electrochemical microscopy. The fabrication procedure is described in detail in order to allow its easy application in other laboratories.

Keywords: Microelectrodes, Nanoelectrodes, Laser puller, Polishing, Cyclic Voltammetry, SECM

1. Introduction

Due to their unequivocal properties [1–4] needle-type nanoelectrodes are increasingly important for applications in scanning electrochemical microscopy (SECM) [5–7], electrochemical STM [8], neuroscience applications [9–11] and as transducers for miniaturized biosensors [12–15]. In order to decrease the size of the active electrode surface below the minimum size of the commercially available noble-metal wires mainly electrochemical etching procedures were described [16–19] leading to conically shaped ultra-microelectrodes. Insulated etched tips were prepared using apiezon wax [20, 21], electrophoretic paint [22–25], electrochemically deposited self-limiting polymer films [26, 27] or poly(ethylene) [28]. Usually, a shrinking of the polymer during a curing step at elevated temperature leads to a protruding conical tip with small dimensions. Such insulated microelectrodes with nanometer-sized active electrode surfaces have been thoroughly characterized by means of cyclic voltammetry [29].

Recently, the use of a laser puller for the fabrication of ultra-microelectrodes was proposed using borosilicate capillaries [30, 31] or Teflon tubes [32] as insulating material. Due to the fast and reproducible local heating of a glass capillary together with an inserted metal wire the metal wire is pulled simultaneously with the glass leading to a drastic decrease of its diameter and a simultaneous tight seal of the metal within the glass capillary. These nanoelectrodes were characterized using SECM approach curves and compared with the theoretically expected negative or positive feedback characteristics [32]. Unfortunately, the exact parameters of the fabrication procedure such as glass type, dimensions of the used glass capillary, parameters of the heating and pulling process have not been disclosed leading to severe difficulties to apply this procedure in other laboratories.

In this article, we present a method for the fabrication and polishing of nanometer-sized disk-shaped microelectrodes. The exact fabrication procedure using a laser puller is described and main focus is on the disclosure of all details to allow the easy transfer of this procedure to other laboratories interested in nanometer-sized disk-shaped electrodes. The obtained nanoelectrodes were characterized by means of electron microscopy, cyclic voltammetry in aqueous and organic electrolyte, and z-approach curves in SECM.

2. Experimental

2.1. Chemicals and Material

All chemicals were used as received from commercial sources. The supporting electrolyte for ferrocene (Janssen Chimica, Geel, Belgium) was 0.1 M tetramethylammonium perchlorate (TMAP, Fluka, Neu-Ulm, Germany) in CH_3CN (Mallinckrodt Baker, Deventer, The Netherlands). For $[Ru(NH_3)_6]Cl_3$ (Strem Chemicals, Newburyport, Ma, USA), the supporting electrolyte was 0.1 M KCl (Merck, Darmstadt, Germany).

Pt-wire with a diameter of 25 μm (purity 99.9%; hard; order number Pt005113/14) was obtained from Goodfellow (Bad Nauheim; Germany). The used quartz-glass capillaries (order number: 1406706) were obtained from Hilgenberg (Malsfeld; Germany) with a length of 100 mm, an outer diameter of 0.9 mm, and an inner diameter of 0.3 mm leading to a wall thickness of 0.3 mm. The silver-filled epoxy glue (EPO-TEK H20S) used to contact the Pt-wire with a Cu-wire (0.25 mm diameter) was purchased from Polytec (Waldbronn, Germany). Alumina polishing suspension with different particle sizes, 1 μm (order number 810-814-300), 0.3 μm (order number 810-827-S) and 0.05 μm (order number 810-826-S) was purchased from Leco Instrumente (Kirchheim, Germany).

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2.2. Equipment

A laser puller (P-2000; Sutter Instrument Company, Novato, CA, USA) was used for the pulling of the microelectrodes. Cyclic voltammetry was performed using a potentiostat (VA-10 with a current-sensitive preamplifier head stage, NPI Electronics, Tamm, Germany) connected to a PC via 16bit AD/DA cards (CIO-DAS 1602/16, CIO-DAC 02/16, Plug-In Electronic, Eichenau, Germany) and controlled by a software specifically programmed in Microsoft Visual Basic 3.0. SECM approach curves were done with a home built instrument which was described previously [33]. Scanning electron microscopy (SEM) was performed in the central facility of scanning electron microscopy of the Ruhr-Universität Bochum by Dr. Rolf D. Neuser using a Gemini 1530 system (LEO, Oberkochen, Germany).

2.3. Nanoelectrode Preparation

A 15 to 20 mm long Pt-wire with a diameter of 25 μm is inserted into a 100 mm long quartz capillary with an outer diameter of 0.9 mm and an inner diameter of 0.3 mm in such a way that the Pt-wire is located in the middle part of the capillary. The quartz capillary is connected with the slays of the laser puller and positioned inside the laser heating chamber so that the laser beam is focused on the center of the glass capillary. Both ends of the capillary are connected to flexible silicone tubes and via a *Y*-connector to a vacuum pump allowing one to evacuate the quartz capillary prior to heating. The laser puller is constantly applying a weak pulling force on the glass capillary in order to detect the viscosity of the glass during heating, which is needed in the conventional pulling process to initiate the hard pull once a predefined viscosity is obtained. However, for the proper cylindrical sealing of the Pt-wire inside the quartz capillary any pulling forces on the glass capillary have to be avoided, and thus the slays of the puller are tightly fixed using a specifically designed clamp.

For cylindrical sealing of the Pt-wire into the glass capillary under reduced pressure, a program which consists of only one line with the following parameter set is loaded, "Heat: 775, Filament: 5, Velocity: 100, Delay: 120, Pull: 1". The program of the laser puller and a stop watch are switched on simultaneously. After 40 s of heating the program of the laser puller is interrupted for a period of 20 s thus allowing the quartz capillary inside the laser puller to cool down and preventing overheating of the laser. This procedure is repeated 5 times to assure an optimal sealing of the Pt-wire inside the quartz glass capillary.

The clamp is then removed immediately and a second program "Heat: 600, Filament: 2, Velocity: 130, Delay: 150, Pull: 220" is activated and started 10 s after the previous program was stopped. After a heating time which varies between 5.6 and 6.2 s the automatic hard pull occurs, leading to the formation of two Pt-nanoelectrodes tightly sealed in glass.

The electrodes are contacted using a Cu-wire (0.25 mm diameter) and silver epoxy (EPO-TEK H20S, Polytec, Waldbronn, Germany).

For polishing newly pulled nanoelectrodes or for repolishing already used ones, a polishing machine was specifically developed. It consists of a cylindrical brass holder which is rotated around its own length axis using a rubber belt and a motor from a rotating disk electrode. The nanoelectrode is inserted into a soft silicone tube and fixed in the center of the brass cylinder in the rotation axis by means of a small screw, which is smoothly pressing the silicone tube at the glass capillary. The cylindrical brass holder can be exactly positioned using micropositioning tables and micrometer screws, which allow especially a slow approach of the very end of the nanoelectrode to the surface of a polishing plate. As polishing plates computer hard-disks have been used as described previously [34]. Polishing is achieved by rotation of the pulled nanoelectrode (5000 rpm) and slowly lowering the electrode tip onto the polishing plate. At the polishing plate a polishing paper or polishing cloth is glued, and polishing can be performed either in a droplet of water or alumina polishing paste (50 nm particle size).

Characterization of the obtained nanoelectrodes was performed by means of cyclic voltammetry in a home-built Faraday cage using a NPI VA-10 potentiostat (2 electrode configuration) with a current-sensitive preamplifier. Assuming a non-recessed, disk-shaped nanoelectrode, estimation of the electrode diameter can be done based on the results from cyclic voltammetry at a scan rate of 50 mV s^{-1} in aqueous 5 mM $[Ru(NH_3)_6]^{3+}$ solution containing 100 mM KCl as background electrolyte. For further investigations cyclic voltammetry at different scan rates was performed in CH_3CN containing 1 mM ferrocene in the presence and absence of 0.1 M TMAP as supporting electrolyte using a chloridized Ag-wire as pseudoreference electrode.

SECM approach curves were performed using an electrode with a radius of 450 nm in 5 mM $[Ru(NH_3)_6]^{3+}$ solution containing 100 mM KCl as supporting electrolyte. For the negative and positive feedback curves the electrode was slowly approached towards a glass and a platinum surface, respectively.

3. Results and Discussion

The reproducible fabrication of Pt-disk electrodes with sub-μm diameter is not possible using commercially available Pt-wires. The intrinsic problem of previously used etching procedures aiming on disk-shaped microelectrodes is the tight insulation of the etched cone and the impossibility to apply polishing procedures maintaining the small electrode surface. Thus, the only possible way which seems to allow a certain degree of reproducibility is the simultaneous pulling of a glass capillary together with a noble-metal wire leading to a significant decrease of the metal-wire diameter, a tight sealing of the metal within the glass sheath and a comparatively wide zone with small metal diameters for later

polishing. It is obvious that this simultaneous pulling process is only possible when the metal wire can be heated to a temperature which is close to its melting point while the glass capillary is still sufficiently stable with respect to its bending by gravity forces. This presupposition implies the use of a laser-based puller, the proper choice of the glass material and of the diameter of the used Pt-wire, and the optimization of the heating and pulling process.

3.1. Fabrication of Pt-Nanoelectrodes by Means of a Laser Puller

If one assumes that the heat transfer inside the glass capillary to the Pt-wire is only achieved by heat radiation (glass is impermeable for IR-radiation) then it becomes immediately clear that the glass walls of the capillary have to be sufficiently thick and the distance between the glass and the Pt-wire should be as small as possible. Thus, in the first step a tight contact between the glass walls of the capillary and the inserted Pt-wire has to be assured, however, simultaneously, the Pt-wire has to be exactly located in the center of the glass capillary. This may be achieved by evacuating the glass capillary during a first heating procedure using a silicone tube connection of both ends of the glass capillary leading via a *Y*-connector to a vacuum pump. Since the used laser puller automatically invokes a hard pull of the capillary when the glass becomes soft during heating a clamp has been designed which prevents the movement of the slays in which the capillary is fixed and adjusted in the laser beam.

In a first heating sequence the evacuated glass capillary is heated 5 times with the laser in the presence of the slay-clamp. A discontinuous heating has been used due to a possible overload of the laser and to keep the glass stiff enough to prevent any bending due to gravity forces. This heating sequence leads to a tight seal between the glass walls and the Pt-wire which is an indispensable prerequisite for a reproducible heat transfer from the glass to the Pt-wire during the following pulling process.

After a cooling time and the removal of the slay clamp, a second heating is performed now allowing the laser puller to invoke the hard pull after detection of a sufficient softening of the capillary. Usually, the two parts of the glass capillary are torn apart at the end of the hard-pull process leading to two Pt-electrodes sealed in glass. As a consequence of this final breaking of the electrodes their surface is often not flat implying the development of a suitable polishing procedure.

3.2. Polishing and Electrical Connection

The Pt-wire inside the quartz capillary is electrically connected by gluing a 250 μm copper wire into the capillary using a two-component silver-filled epoxy glue. For polishing, the electrode is fixed inside a cylindrical brass holder along the rotation axis using a soft silicone tube and a screw. By means of a rubber band the brass holder is rotated at 5000 rpm and slowly lowered down onto the surface of a polishing plate using manual micropositioning elements. Due to their flatness and height tolerance, old computer hard disks are used as polishing plates. Polishing can be either performed in a drop of water on a polishing paper or in a drop of a 50 nm particle size alumina paste on a soft polishing cloth. The polishing set-up is schematically shown in Figure 1.

As a matter of fact, the polishing process has a significant impact on the final size of the disk electrode, and especially for nanoelectrodes with diameters smaller than 100 nm the polishing has to be done very carefully. However, as compared with conically etched microelectrodes the length of the pulled part of the wire is rather long causing a far less dramatic increase of the electrode size by the polishing procedure.

In addition, due to the extremely small diameter at the very end of the microelectrode, a precession of the tip in a circle on the polishing paper appears depending on the electrode-to-polishing plate distance. This precession leads to a predominant polishing of the outer side of the glass capillary thus decreasing the diameter of the insulating glass sheath around the disk-shaped active electrode area. Furthermore, this conical polishing of the glass sheath can be even more improved by changing the angle between the rotation axis of the microelectrode and the surface of the polishing plate.

The overall electrode fabrication process is schematically shown in Figure 2.

As a matter of fact, since the exact length of the Pt-wire inside the quartz capillary, the reproducibility of the sealing and pulling process, and the polishing procedure are varying between the electrodes, the exact size of the obtained nanoelectrode has to be electrochemically determined.

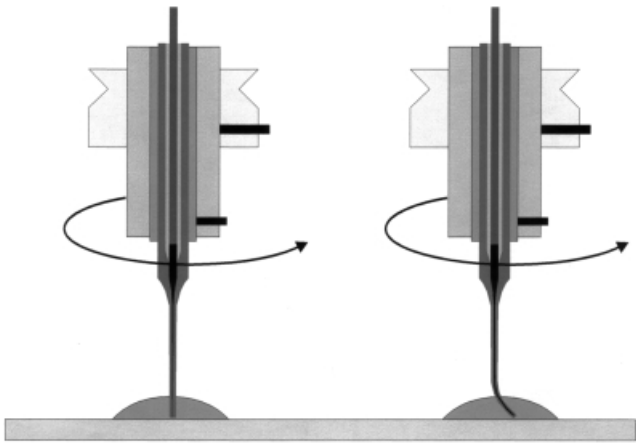

Fig. 1. Schematical representation of the set-up for nanoelectrode polishing. Left: Polishing by rotation of the nanoelectrode on a polishing plate in a drop of water or alumina suspension. Right: Precession of the fragile electrode tip after pressing the electrode tip onto the polishing plate leads to a conical polishing of the insulating glass sheath.

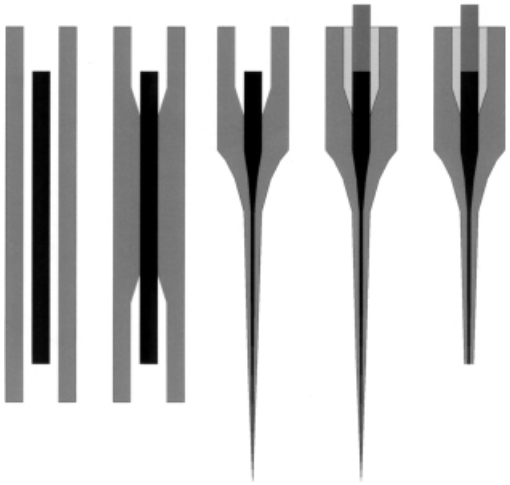

Fig. 2. Step-by-step summary of the microelectrode fabrication process (left to right): insertion of the Pt-wire into the glass capillary; cylindrical melting of the quartz glass to invoke contact between glass and Pt-wire concomitantly assuring the positioning of the Pt-wire in the center of the glass capillary; simultaneous pulling of quartz capillary and Pt-wire; contacting of the Pt-wire by means of a Cu-wire and a Ag-filled epoxy glue; polishing of the obtained microelectrode.

3.3. Nanoelectrode Characterization

The obtained nanoelectrodes have been characterized by means of SEM, cyclic voltammetry and SECM approach curves. In Figure 3 a SEM image of a pulled nanoelectrode is shown. One can clearly see the extremely fast decrease of the quartz diameter at the beginning of the heating zone. The length of the pulled shaft is typically about 15 mm.

Looking with the SEM at higher magnification at the front end of the pulled glass capillary after polishing one can clearly identify the active electrode disk right in the center of the insulating glass sheath (Fig. 4a). In addition, the conical polishing of the surrounding glass due to the precession of the pulled fiber on the polishing plate can easily be seen. At an even higher magnification the radius of the electrode surface can be determined to be about 200 nm in this case (Fig. 4b).

Assuming the geometry of the nanoelectrodes to be disk shaped, the radius of the electrochemical active surface of the nanoelectrodes can be determined from the diffusion limited steady state current, using Equation 1

$$i = 4nFDcr \tag{1}$$

where n is number of electrons transferred per molecule, F is the Faraday's constant, D and c the diffusion coefficient and bulk concentration of the electroactive species, respectively, and r the radius of the electroactive electrode surface.

The size of the electrochemically active surface of a set of laser-pulled Pt-nanoelectrodes was determined by means of cyclic voltammetry in a 5 mM $Ru(NH_3)_6^{3+}$ ($D = 0.548 \times 10^{-5}$ $cm^2\ s^{-1}$ [35, 36]) solution containing 0.1 M KCl (Fig. 5).

Using the described nanoelectrode fabrication procedure, well-defined cyclic voltammograms at a scan rate of 50 mV s^{-1} were obtained, showing an ideal sigmoidal shape for various radii in the range from 900 to 10 nm.

The cyclic voltammograms show comparatively small deviations due to Ohmic resistance or overlaying capacitance, even for the smallest electrodes with diameters down to 10 nm indicative for the high quality of the electrical connection of the Pt-wire inside the quartz capillary by

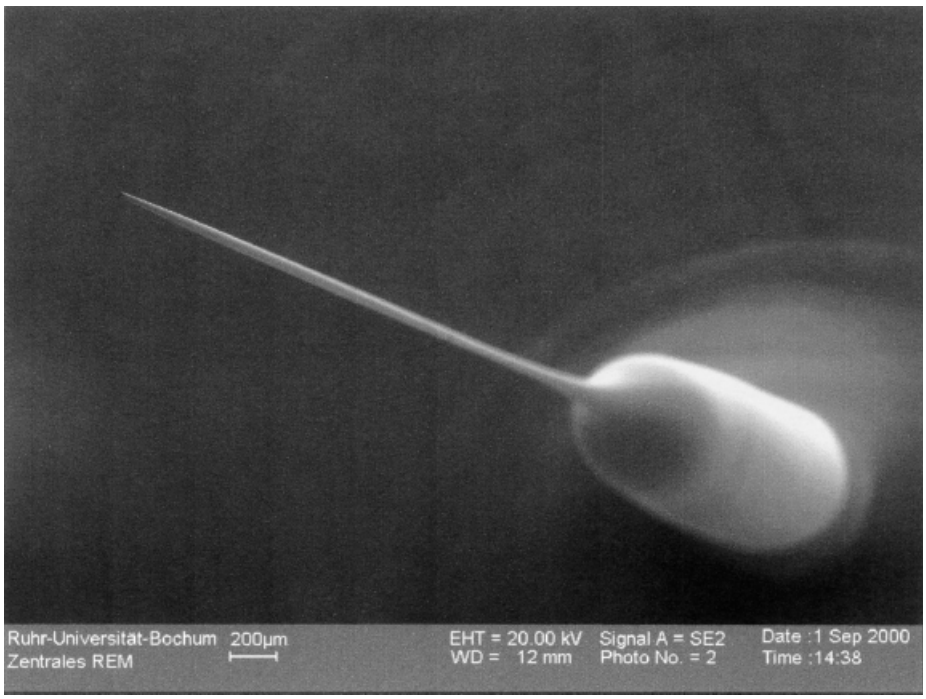

Fig. 3. SEM-image of a pulled Pt-disk nanoelectrode.

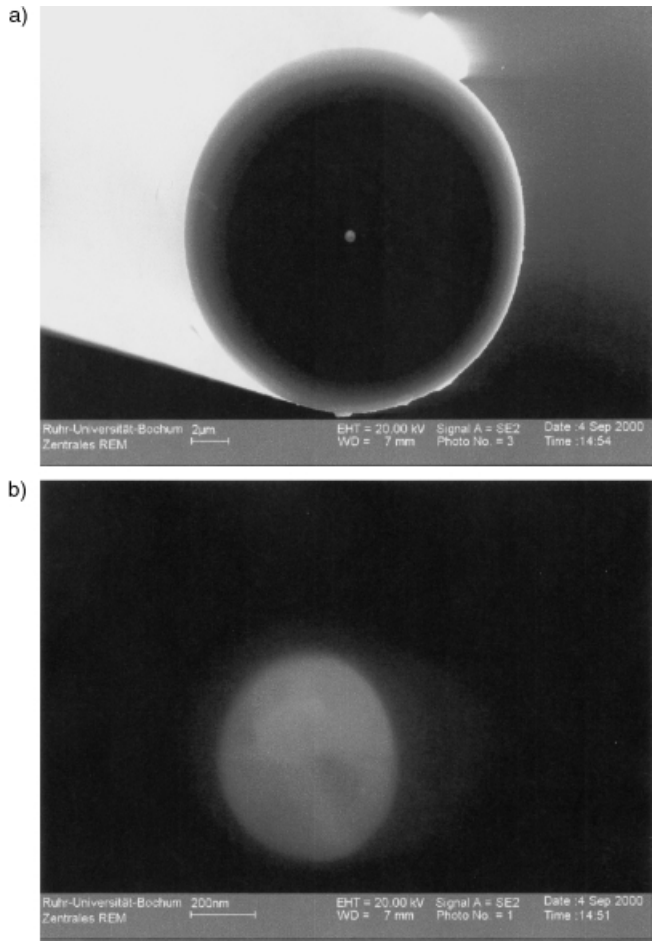

Fig. 4. a) SEM image of the front end of a pulled nanoelectrode as shown in Figure 5. The light point in the center is the active Pt-disk which has been unequivocally proved by means of EDX. b) Active Pt-disk of the same microelectrode at higher magnification.

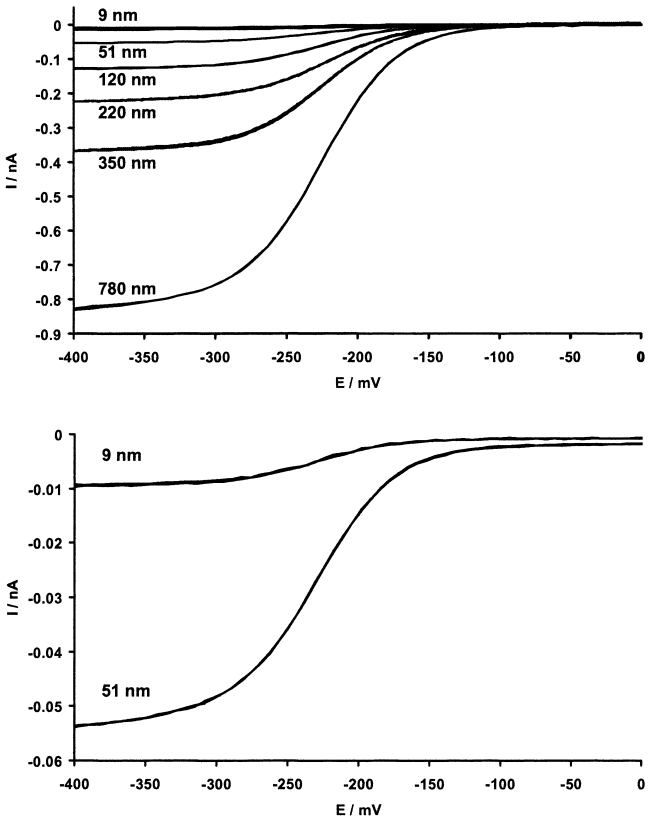

Fig. 5. Cyclic voltammograms of a 5 mM $[Ru(NH_3)_6]^{3+}$ solution containing 0.1 M KCl as supporting electrolyte performed with a set of Pt-nanoelectrodes obtained by the proposed pulling process. The calculated disk radii are used to distinguish the different electrodes (scan rate 50 mV s^{-1}). a) nanoelectrodes with radii from 780 nm to 9 nm. b) nanoelectrodes with radii of 51 nm and 9 nm with magified current axes.

means of the Ag-filled epoxy glue. However, to demonstrate that the obtained nanoelectrodes show the expected negligible capacitance and Ohmic resistance cyclic voltammograms at different scan rates were recorded in CH_3CN containing ferrocene as electroactive species in the presence and absence of TBAP as supporting electrolyte (Fig. 6).

The sigmoidal shape of the cyclic voltammograms remain unchanged and the diffusion limited current is unaffected by the scan rate. With the exception of a potential shift caused by the *iR*-drop between the pseudo-reference electrode and the working electrode the shape of the cyclic voltammograms remain unchanged even in the absence of supporting electrolyte. A slight increase in the capacitance can be observed with faster scan rates leading to the small separation of the current traces for the oxidative and reductive half-scan which can, however, not be separated from the overall capacity of the whole measuring set-up at these small currents below 1 pA.

Using Equation 1 and a diffusion coefficient for ferrocene of $D = 2.47 \times 10^{-5}$ cm^2 s^{-1} [35, 36] a radius of 6 nm for the used nanoelectrode can be determined.

In order to further characterize the obtained nanoelectrodes Z-approach curves were recorded in a SECM. A nanoelectrode was characterized by means of cyclic voltammetry in a 5 mM $[Ru(NH_3)_6]^{3+}$ and its radius was determined to be 450 nm using Equation 1. The approach of the 450 nm radius electrode towards a Pt-surface shows the expected current increase due to the positive feedback (Fig. 7a) while the approach towards an insulating glass surface shows the typical negative feedback effect (Fig. 7b).

Comparison of the approach curves with the calculated current-distance behavior obtained following the equations proposed by Mirkin et al. [6] (lines in Fig. 7) show a good agreement between the experimental and calculated current values indicative for a disk-shaped electrode geometry.

4. Conclusions

Using the proposed nanoelectrode fabrication procedure and the parameters as specified above nanoelectrodes with diameters below 1 µm were routinely prepared. A polishing procedure was developed, and the obtained microelectrodes were characterized by means of cyclic voltammetry in

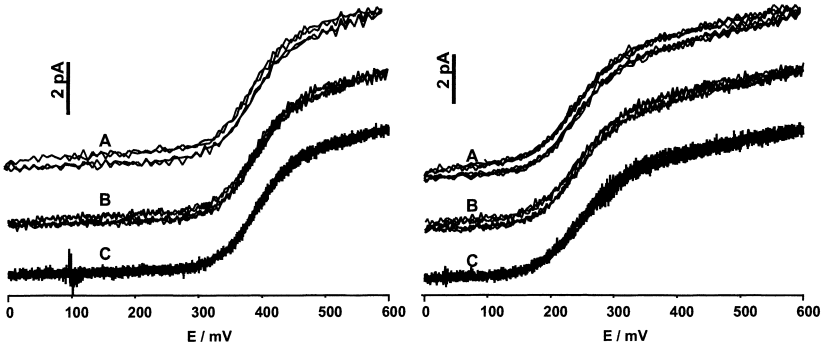

Fig. 6. Cyclic voltammograms of 1 mM ferrocene in CH_3CN in the presence (left) and absence (right) of 100 mM TMAP as supporting electrolyte. The nanoelectrode had a radius of about 6 nm. Scan rates: A) 100 mV s^{-1}; B) 50 mV s^{-1}; C) 10 mV s^{-1}.

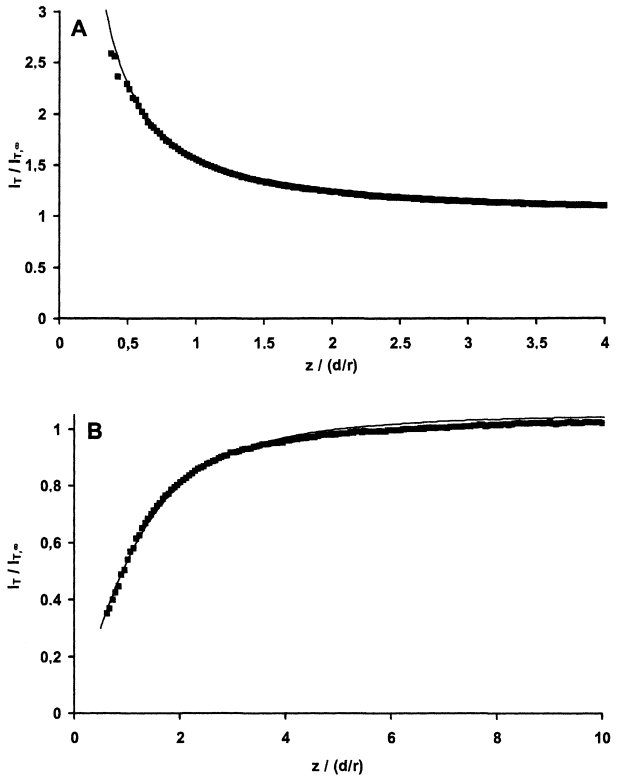

Fig. 7. Normalized current vs. normalized distance curves obtained with a 450 nm radius electrode during its approach to a Pt-surface (A: positive feedback) and glass surface (B: negative feedback) in a SECM (aqueous 5 mM $[Ru(NH_3)_6]^{3+}$ solution containing 100 mM KCl). The curves are compared with the theoretical approach curve calculated as described in [6].

aqueous and organic electrolyte, SEM images, and SECM approach curves. The smallest electrodes obtained so far have radii below 10 nm. However, due to small variations, e.g., in the time for removing of the puller-slay clamp, in the length and position of the Pt-wire inside the glass capillary, and especially in the degree of polishing the exact diameter of the nanoelectrodes needs to be determined by cyclic voltammetry.

Future work will be focused on the application of these nanoelectrodes for high-resolution imaging in scanning electrochemical microscopy.

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6. References

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